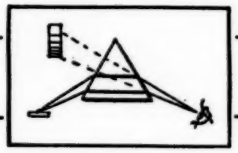
Journal of the OPTICAL SOCIETY *of* AMERICA

VOLUME 33
NO. 1



JANUARY
1943

Volume Title Page 1

Investigations on the Intrinsic Properties of the Color Domiain. II . . . . . L. SILBERSTEIN 1

Adaptation in Color Space . . . . . DOMINA EBERLE SPENCER 10

Specification of Small Chromaticity Differences . . . . . DAVID L. MACADAM 18

Applications of Near Infra-Red Spectrophotometry . . . . . E. I. STEARNS 27

Method for Determining Depolarization Factors in Raman Spectra . . . . . D. H. RANK, R. J. PFISTER, AND H. H. GRIMM 31

On Size-Frequency Distribution in Photographic Emulsions . . . . . LUDWIK SILBERSTEIN 35

Propagation of Radiation in a Scattering and Absorbing Medium . . . . . E. O. HULBERT 42

Electronic Voltage Regulator for Precise Densitometric Measurements . . . . . H. W. DIETERT AND M. F. HASLER 45

Preparation of Purified Inorganic Compounds for Use in Spectrographic Standards . . . . . RAY C. HUGHES 49

Published monthly
at Prince and Lemon Sts., Lancaster, Pa.
by the
AMERICAN INSTITUTE OF PHYSICS
Incorporated
175 Fifth Avenue, New York, N. Y.
FOR AND UNDER THE EDITORIAL SUPERVISION OF THE
OPTICAL SOCIETY OF AMERICA

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Cumulative Index, 1917–1935: **$2.00**

Subscriptions, renewals and orders for back numbers should be addressed to Prince and Lemon Streets, Lancaster, Pennsylvania, or to the American Institute of Physics, 175 Fifth Avenue, New York.

The *Journal of the Optical Society of America* is published monthly at Prince and Lemon Streets, Lancaster, Pennsylvania.

Entered as second-class matter March 22, 1933, at the Post Office at Lancaster, Pennsylvania, under the Act of March 3, 1879. Acceptance for mailing at special rate of postage provided for in the Act of February 28, 1925, embodied in paragraph 4, section 538, P. L. and R., authorized March 22, 1933.

Journal of the
OPTICAL SOCIETY
of AMERICA

VOLUME 33 JANUARY, 1943 NUMBER 1

Investigations on the Intrinsic Properties of the Color Domain. II *

L. SILBERSTEIN
Kodak Research Laboratories, Rochester, New York
(Received October 24, 1942)

THE main and, perhaps, most valuable result of Dr. MacAdam's recent investigations,[1] implying many thousand color matchings, consists of twenty-five closed curves spread all over the color triangle, with the conventionally adopted stimuli-coordinates x, y as Cartesian coordinates, each curve representing the locus of colors at a constant "distance" or just perceptible chromaticity difference,† $ds=1$. Now, each of these curves has turned out, with a fair approximation, to be an *ellipse* and, is therefore, expressible by the quadratic form:

$$ds^2=g_{11}dx^2+2g_{12}dxdy+g_{22}dy^2 \qquad (1)$$

equated to a constant (conventionally, 1), with the coefficients g_{11}, g_{22} both positive and $g_{12}^2<g_{11}g_{22}$.

This result itself is of fundamental importance for our knowledge of the intrinsic structure of the color domain. It establishes the color distance element (or "line-element"), so far established only for equiluminous colors, as what is technically called a *definite positive quadratic differential form* of the coordinates, a property assumed by the present writer[2] and by all investigators since the time of Helmholtz, but only now proved experimentally. If those twenty-five closed curves, or most of them, turned out to be cubic ovals, say, or curves of yet higher degree, in the adopted system x, y, Helmholtz's original claim or hypothesis would be contradicted, and the line-element could not be reduced to a quadratic differential form by introducing any other system of coordinates whatever.

In other words, MacAdam's assemblage of ellipses establishes the twofold of equiluminous colors (at least, as seen by P. G. Nutting, Jr.) as isomorphous with, i.e., correctly representable by, a geometric surface, *viz.*, a surface defined by the quadratic differential form (1) with its experimentally determined coefficients g_{ik}. We shall speak hereafter of such a surface as the "true color surface."

In fact, the values of these coefficients at the color-centers of the aforementioned ellipses are determined completely by the size, the shape, and the orientation of these ellipses. If a, b are their principal semi-axes and θ is the inclination of the former to the x axis of the color chart, it is readily found that

$$\begin{aligned} g_{11}&=(\cos^2\theta/a^2)+(\sin^2\theta/b^2),\\ 2g_{12}&=\sin 2\theta[(1/a^2)-(1/b^2)], \qquad (2)\\ g_{22}&=(\sin^2\theta/a^2)+(\cos^2\theta/b^2). \end{aligned}$$

The coefficient g_{12} vanishes wherever $\theta=0$ or $\pi/2$ (which is nearly enough the case for just

* Communication No. 658-II from the Kodak Research Laboratories.

[1] D. L. MacAdam, J. Opt. Soc. Am. **32**, 247–274 (1942).

† This difference, to be called *unit distance*, is ultimately measured by the standard deviation of matching the central color in various directions.

[2] L. Silberstein, J. Opt. Soc. Am. **28**, 63–85 (1938).

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one of the ellipses). In crossing the line $g_{12}=0$, the coefficient g_{12} changes its sign in an obvious way.

By means of these formulas* MacAdam has computed, from the observed a, b, θ, the values of the three coefficients at the twenty-five points of the color chart mentioned. The values of each of the coefficients in various regions of the color twofold differ from each other very considerably, as could also be expected from the diversity of the original ellipses. By graphical interpolation, MacAdam has drawn, on separate sheets, a whole system of curves of constant g_{11}, of constant g_{12}, and of constant g_{22}. Each of these systems of curves is extremely complicated as to form and distribution of values, resembling rather a topographic map of some very rugged territory, so that the derivation of the form of the g_{ik} from these drawings as mathematical functions of x, y, is wholly out of the question. One has to be content with the knowledge of their numerical values at so many discrete places or (by interpolation) along certain lines.

Now, such being the case, we shall seek to find at least some intrinsic properties of the true color surface, that is to say, of the geometrical surface whose distance element is represented by (1) with the g_{ik} thus specified numerically. Needless to say, such a surface would have the property of representing correctly the chromaticity difference of any two colors by the distance (measured along the geodesic of the surface) between the points corresponding to these two colors. Those twenty-five ellipses, for example, would instantly become circles on that surface, all, moreover, of the same (unit) radius. Some students of colorimetry (e.g., D. B. Judd)[3] have assumed for simplicity that the plane itself is such a surface and that to make distances on a plane chart proportional to chromaticity differences it is enough only to replace x, y by some simple, nay bilinear, functions of x, y. Such, however, can scarcely be the case; the true color surface is hardly a plane, that is, the Gaussian curvature** of the twofold defined by the observed g_{ik} showing such a highly complicated distribution is not at all likely to vanish everywhere. Nay, it is even extremely unlikely that the curvature should have any constant value over all the contemplated color twofold.

I have shown elsewhere[2] that there are reasons to believe that the twofold of equiluminous colors is a rather complicated surface of *variable curvature*. Since my deductions, however, were based upon the assumption of some kind of a generalized Fechner law whose validity is rather doubtful, I do not consider them convincing.

To avoid hypotheses, the surest way of forming an idea of the true color surface is to derive its properties from the observed distribution of the coefficients g_{ik} (technically, the components of a genuine covariant *tensor* of rank two), now made available through MacAdam's work. By "properties" are meant, of course, properties of the true color surface which are independent of the choice of the system of color coordinates.

We shall now proceed to develop a few simple relations which will lead to some such properties and, perhaps, to a bodily construction of the true color surface itself.

Of paramount importance is the *determinant* g of the metrical tensor, i.e., $\begin{vmatrix} g_{11} g_{12} \\ g_{21} g_{22} \end{vmatrix}$, and since $g_{12}=g_{21}$,

$$g=g_{11}g_{22}-g_{12}^2,$$

which, as we saw before, is positive throughout the color twofold. This determinant is *not* itself an invariant. It changes, in general, in passing from one coordinate system x, y to another, x', y', but it has this cardinal (and well-known) property that the product of its square root into $dxdy$, integrated over any domain, is invariant with respect to any coordinate transformations whatever, that is to say,

$$\int (g)^{\frac{1}{2}} dxdy = \int (g')^{\frac{1}{2}} dx'dy'.\dagger$$

This general invariant certainly expresses an intrinsic property of the domain included by the integration. It is, apart from a conventional constant numerical factor, the true *area* of the domain represented by any closed portion of, say, the plane x, y chart, that is, the area of the portion of the true color surface corresponding

* Derived by him, independently of the writer.

[3] D. B. Judd, J. Opt. Soc. Am. **25**, 24–35 (1935).

** This is an *invariant* with respect to any transformations of the coordinates whatever, not only bilinear ones.

† A simple proof, not only for two, but for any number of dimensions, may be found in the writer's *Theory of Relativity* (London, 1924), second edition, chapter 12.

to this portion of the chart. In particular, the true area of any elementary figure (that is, within which g does not change appreciably), of chart-area σ', is

$$\sigma = g^{\frac{1}{2}}\sigma'.$$

E.g., the charted area of an elementary rectangle dx, dy is $\sigma' = dxdy$, and its true area, $\sigma = g^{\frac{1}{2}} \cdot dxdy$. Such "elementary" figures are MacAdam's ellipses themselves. The charted area of any of these ellipses being πab, its true area will be

$$\sigma = \pi ab \cdot g^{\frac{1}{2}}.$$

Clearly, the determinant g will give us an important piece of information for passing from the color chart to the true color surface. For $g^{\frac{1}{2}}$ is the ratio in which the portion σ' or any element of the chart must be magnified (or reduced) in order to be made an element of the true color surface.

Let us therefore evaluate the determinant in terms of the measured attributes of the ellipses. By the definition of g and by (2), we have

$$g = [(\cos^2\theta/a^2) + (\sin^2\theta/b^2)] \times [(\sin^2\theta/a^2) + (\cos^2\theta/b^2)] - \sin^2\theta\cos^2\theta[(1/a^2) - (1/b^2)]^2.$$

The fourth powers of $1/a$, $1/b$ cancel out and we are left with

$$g = (1/a^2b^2)[\sin^4\theta + \cos^4\theta + 2\sin^2\theta\cdot\cos^2\theta] = [(\sin^2\theta + \cos^2\theta)^2/a^2b^2] = 1/a^2b^2,$$

so that the required magnification ratio has the remarkably simple form

$$g^{\frac{1}{2}} = 1/ab, \tag{3}$$

much simpler than that of the three components of the tensor.

The true area of any of the charted ellipses now becomes

$$\sigma = \pi ab/ab = \pi,$$

equal for all ellipses, as it should be. For to all these ellipses should correspond, on the true color surface, elementary circles of unit radius.

The knowledge of the magnification ratio of areas does not, however, by itself suffice for building up the true color surface. We must also know the shape to be given to each element of area in passing from the chart to that surface.

Now, the true length of any linear element whose charted components are dx, dy is ds itself as expressed by (1). Thus, the true lengths of the sides dx, dy of any rectangle of the chart are, respectively,

$$g_{11}^{\frac{1}{2}}dx, \quad g_{22}^{\frac{1}{2}}dy. \tag{4.1}$$

The true angle ω between them is, in general, no longer a right angle. It is given by a well-known formula of differential geometry. But since we already know the expression for the true area, we can easily derive from it and from (4.1) the formula for ω. In fact, the true area of the charted rectangle is, on the one hand, $g^{\frac{1}{2}}dxdy$, and on the other hand,

$$g_{11}^{\frac{1}{2}}dx \cdot g_{22}^{\frac{1}{2}}dy \cdot \sin\omega.$$

Thus, the required angle is given by

$$\sin\omega = (g/g_{11}g_{22})^{\frac{1}{2}} = [1 - (g_{12}^2/g_{11}g_{22})]^{\frac{1}{2}},$$

so that we have, at the same time,

$$\cos\omega = g_{12}/(g_{11}g_{22})^{\frac{1}{2}}. \tag{4.2}$$

We see that ω is a right angle only where g_{12} vanishes, i.e., where the axes of MacAdam's ellipses are parallel to the coordinate axes of the chart.

In fine, then, the element of the true surface corresponding to any infinitesimal rectangle $dxdy$ of the chart is a *parallelogram* whose sides and angle are determined completely by (4.1) and (4.2) in terms of the local values of the g_{ik}. The same thing holds, practically, for any finite but sufficiently small rectangles $(\Delta x \cdot \Delta y)$, within which, that is, the g_{ik} do not change appreciably.

By means of these elementary relations, the true color surface may actually be constructed first, as a paper model, and then, perhaps, cast in plaster, as follows:

Cut up the plane color triangle, upon which the values of g_{11}, g_{22}, g_{12} are charted, into a number of small rectangles, say squares. Use for each whole square the values of the g_{ik} prevailing, say, at its center. Then each square will have to be shaped into a perfectly definite parallelogram, in accordance with (4.1) and (4.2). Suppose all these parallelograms are drawn on paper and cut out. In order to construct the true color surface, we have only to glue them together in the proper way. A side originally

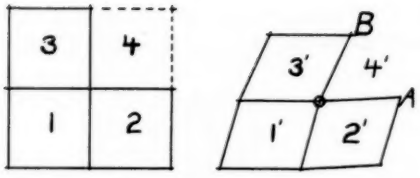

FIG. 1. Method of assembling parallelograms to construct true color surface.

common to two squares must be shared by the two corresponding parallelograms, and so also a corner common to four squares must be shared by the four corresponding parallelograms. Since the values of g_{11} (say) in two adjacent squares differ from each other, the two sides which are to be made congruent will differ from each other somewhat in length; but since the variation of the g_{ik} from square to square is supposedly slow, these differences will call only for some slight trimming down of the separate parallelograms before assembling them. This readjustment ought not to entail any serious difficulties. Let three adjacent squares, 1, 2, 3, not in a line (see Fig. 1), give rise, after a proper trimming down, to the connected triad of parallelograms 1′, 2′, 3′. Whatever their shapes, we can always spread the whole triad on a plane. Now, however, let the square 4 be transformed into the proper parallelogram. It may happen that its angle ω will differ from AOB in the plane. If so, then the elements 2′ and 3′ will have to be bent out of the plane one way or the other so as to ensure the proper fitting of the element 4′. This, then, will be our first token that the "true surface" is not a plane, nor developable upon a plane.

In such manner we can proceed with the structure until all the parallelograms (arising from as many squares) have been fitted into their proper places. This, then, will give us the required surface.*

The objection may be raised that at some stage of this building-up (or "assembling") process a situation may arise in which a new parallelogram cannot, in our actual (Euclidean) space be fitted at all into the structure already accomplished (even with the explained tolerance necessitated by the finite, though small, variations of the g_{ik} from square to square). Such a situation, however, can never arise. For, by a well-known theorem, any manifold of n dimensions defined by its line-element,

$$ds^2 = g_{ik}dx_i dx_k$$

(to be summed over i, k from 1 to n), can always be embedded in a Euclidean space of (at the utmost)

$$m = (n/2)(n+1)$$

dimensions, no matter what the particular form of the g_{ik} as functions of the coordinates $x_1, x_2, \cdots x_n$. Thus, e.g., a threefold ($n=3$) cannot, in general, be embedded in a Euclidean space of less than six dimensions. What, however, interests us here is a twofold ($n=2$), and for this we have, fortunately, $m = 2 \cdot 3/2 = 3$, so that a twofold defined by any (positive) quadratic form (1) can certainly be embedded in a three-dimensional Euclidean space, and thus constructed in our own space. It is, of course, another question whether the surface thus built up will be developable, at least approximately, upon a plane or not.

It may be well to illustrate the proposed method of surface construction by a very simple example.

Let the given tensor components be

$$g_{11} = \cos^2 y, \quad g_{12} = 0, \quad g_{22} = 1,$$

or, the line-element, $ds^2 = \cos^2 y \cdot dx^2 + dy^2$. Let our chart be again a plane sheet of ordinary squared or "graph" paper with x and y as Cartesians measured horizontally and vertically. By (4.1), the "true length" of any vertical segment Δy is Δy itself and that of a horizontal segment Δx, placed at a height y, $\Delta x \cdot \cos y$. By (4.2) and, since $g_{12} = 0$, the true angle ω belonging to the charted right angle (dx, dy) is again a right angle. In fine, every small square** of the chart is to be reduced to a rectangle of unchanged height, but with the width multiplied by the local $\cos y$. Since, moreover, Δy remains unchanged, we need not cut up the chart into separate squares, but may deal at once with a whole vertical column of small squares, ranging from $y=0$ to $y=\pi/2$, as shown in Fig. 2, where

* As a paper polyhedron of so many plane faces, to be sure. If this is cast in plaster, the model may be polished down to a smooth surface.

** Within which, that is, we are willing to disregard the changes of $\cos y$.

one scale unit is used for 10° (or $\pi/18$) of y as well as of x and where the treatment of two such columns is shown. These are reduced laterally, by the factor $\cos y$, to the two shaded strips. If this pair of strips is cut out and their inner edges are brought into contact, they will automatically bend out of the plane and form a portion of the required surface, to wit, $\frac{1}{18}$th of a hemisphere, their vertices coalescing at the pole and their bases forming this fraction of the equator. Thirty-six such strips would give a hemisphere and, if repeated below the x axis, the complete sphere.

The application of the proposed method to this case was easy, mainly because the original rectangular chart elements remained rectangular ($g_{12}=0$), instead of being deformed into various parallelograms, as in the above treatment of the color twofold. (A further, but not so important, simplification was introduced by the invariability of dy or $g_{22}=\text{const.}=1$.)

Now, an analogous simplification of the construction method may be secured for our color twofold by utilizing a certain curvilinear network. (This network is interesting also for its own sake.)

This concept can be briefly defined and explained as follows:

The twenty-five observed ellipses endow each of as many points of the color triangle with a definite orthogonal pair of directions, *viz.*, those of the principal axes of the local ellipse or, in fact, the principal axes of the colorimetrical tensor, g_{ik}.† Now, just as in the familiar construction of the lines of magnetic force from a number of orientations of a magnetic needle, let us draw a set of what we may call a lines, i.e., curves everywhere tangential to the major axes, and similarly a set of b lines tangential to the minor axes of the ellipses. This implies of course some graphical interpolation and thus guesswork, but does not leave much freedom.

Such a system of a lines and b lines, drawn through the aforementioned twenty-five points, is shown in Fig. 3.

This system of lines is considerably simpler and more regular than any of the three graphs of the $g_{ik}=\text{const.}$ mentioned before; this was to be expected, for the principal axes of a tensor have a more intrinsic meaning than its components with respect to an arbitrary framework of coordinates.

To begin with, by its very construction, the system of a lines and b lines is strictly orthogonal on our chart. But this property goes deeper. Let $d\xi$ and $d\eta$ be the elements of length measured on the chart along the a lines and the b lines, respectively. Then the distance-element (1) assumes the form

$$ds^2=(d\xi^2/a^2)+(d\eta^2/b^2)\equiv\gamma_{11}d\xi^2+\gamma_{22}d\eta^2, \quad (5)$$

which (with $ds=\text{const.}$) is in fact the original equation of the observed ellipses. The tensor is now reduced to

$$\gamma_{11}=1/a^2, \quad \gamma_{22}=1/b^2, \quad \text{and} \quad \gamma_{12}=0$$

(its determinant is simply $\gamma=\gamma_{11}\gamma_{22}=1/a^2b^2=$ to the previous g), so that, by (4.1) and (4.2), the true lengths of the elements $d\xi$, $d\eta$ are $d\xi/a$, $d\eta/b$, and the true angle (ω) between them is again a right angle.

In other words, the charted network of a lines and b lines (Fig. 3) represents an *orthogonal system* of lines on the true color surface* and

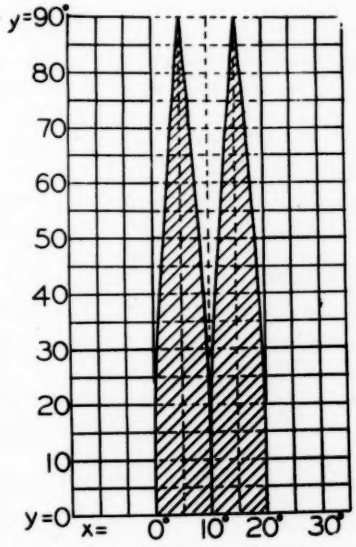

FIG. 2. Example of construction of curved surface (a sphere: $ds^2=\cos^2 y\cdot dx^2+dy^2$) out of parallelograms.

† Which has all the properties of Hamilton's linear vector operator, in two dimensions.

* While (as we saw) the orthogonal net of x and y lines of the chart did not represent an orthogonal system of the color surface.

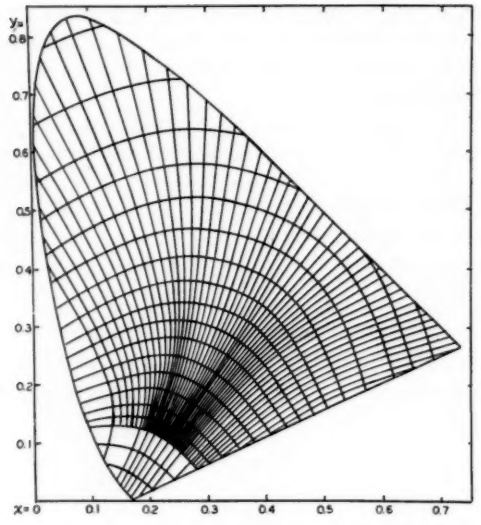

FIG. 3. Curvilinear coordinate system defined by directions of major and minor axes of noticeability ellipses.

thus expresses an actual property of the color twofold.

The application of the proposed method of surface construction is now much simpler. Let the chart, on a larger scale, be cut up into a number of sufficiently small meshes of the a, b network. Each of these rectangular meshes has now to be reduced to a *rectangle* of sides $d\xi/a$, $d\eta/b$, and in order to construct the surface one has only to put all these rectangles together as explained before. The technical difficulties of the process will thus be considerably alleviated.

In the meantime, the plane color triangle with the a, b network spread over it and with the measured and interpolated a values and b steps indicated as in Fig. 4 can render, practically, almost as good services as would a true color surface.

It may be worthwhile, therefore, to survey the properties of this charted network in connection with the associated line-element (5).

The relations between $d\xi$, $d\eta$ and the original dx, dy are

$$\begin{aligned} d\xi &= \cos\theta\cdot dx+\sin\theta\cdot dy,\\ d\eta &= \sin\theta\cdot dx-\cos\theta\cdot dy, \end{aligned} \tag{6}$$

corresponding simply to a local rotation θ of the coordinate axes. This is the reason why the determinant of the tensor (not a general invariant) has retained its value, $\gamma=g=1/a^2b^2$. The tensor has just one more invariant with respect to such particular transformations, namely, $g_{11}+g_{22}$; and, in fact, we now have directly

$$\gamma_{11}+\gamma_{22}=(1/a^2)+(1/b^2),$$

and so also, by (2),

$$g_{11}+g_{22}=(1/a^2)+(1/b^2).$$

Along an a line we have $dy/dx=\tan\theta$, so that, by (6) $d\eta=0$, and along a b line, $dy/dx=-\cot\theta$, $d\xi=0$.

Since θ, the inclination of the major axis, varies from place to place, $d\xi$ and $d\eta$ are not, in general, total differentials of functions of position. The necessary and sufficient conditions for $d\xi$ and $d\eta$ to be total differentials are

$$\partial\cos\theta/\partial y=\partial\sin\theta/\partial x$$

and

$$\partial\sin\theta/\partial y=-\partial\cos\theta/\partial x,$$

or

$$\cos\theta(\partial\theta/\partial x)+\sin\theta(\partial\theta/\partial y)=0,$$

$$\sin\theta(\partial\theta/\partial x)-\cos\theta(\partial\theta/\partial y)=0.$$

Since the determinant of these two equations does not vanish, they imply necessarily $\partial\theta/\partial x=0$ and $\partial\theta/\partial y=0$ or $\theta=$constant. Thus, we see that both $d\xi$ and $d\eta$ would be, rigorously, total differentials if, and only if, all a lines were straight lines parallel to each other. Now, as will be apparent from Fig. 3, such is nearly enough the case in certain more or less extended regions, but not all over the color triangle. In spite of this, an a line is characterized locally by $\eta=$const. and a b line by $\xi=$const., so that ξ, η remain convenient local coordinates. We have only to keep in mind that η retains its value if we pass from one point to another point of the same a line *along* this line, but not by a detour. The use of the a, b network as such can never lead to misconceptions or inconsistencies.

In terms of ξ, η the curvature K of the true color surface, which in x, y has a very unwieldy expression, assumes a comparatively simple form, to wit, up to small terms due to the slow variation of θ from place to place,

$$K=ab\{(\partial/\partial\xi)[(a/b^2)(\partial b/\partial\xi)] +(\partial/\partial\eta)[(b/a^2)(\partial a/\partial\eta)]\}. \tag{7}$$

This would vanish if, for instance, a depended only on ξ (i.e., varied only along the a lines) and b only on η*; such, however, is not even nearly the case; the a and b vary also transversally. Nevertheless, the curvature of the color surface might vanish, namely, if the bracketed expression or, with $\alpha'=1/a$, $\beta'=1/b$, the expression

$$(\partial/\partial\xi)[a(\partial\beta'/\partial\xi)]+(\partial/\partial\eta)[b(\partial\alpha'/\partial\eta)]$$

happened to vanish.

The curvature of the color twofold, as given by (7), may be evaluated numerically at several places of the color triangle, by means of the distribution of a, b values represented graphically in Fig. 4. In this chart, the dotted lines are loci of constant a, e.g., $a=0.004$, 0.005, etc., as marked along the spectrum, and the values of the minor axis b are proportional to the (charted) distance β between successive a lines, to wit,

$$b=\tfrac{1}{10}\beta.$$

Thus, in terms of a, β,

$$K=K_1+K_2,$$

where

$$K_1=-a\beta(\partial/\partial\xi)[a(\partial/\partial\xi)(1/\beta)]$$

and

$$K_2=-(a\beta/100)(\partial/\partial\eta)[\beta(\partial/\partial\eta)(1/a)].$$

Before proceeding to numerical evaluations, notice that the dimensions of our ξ, η are the same as those of a, b, or K, a pure number. The reason is obvious. Actually, the curvature of the color twofold has the dimensions of the reciprocal square of a chromaticity step,** but such a "step" has, from the beginning, been simply set equal to 1. (So also is the true area or the content of any of the ellipses just π, a pure number.)

In fine, the curvature K of the *color twofold* is, in our reckoning, a pure number. The curvature of its geometrical model, the true color *surface*, will of course have the dimensions of a reciprocal squared length. If, e.g., this model is built on such a scale that one "step" is represented by 1 cm, the curvature of the model at any place will be K cm^{-2} (where K is the pure number stated). At the same time, the area, on this model surface, of any of the circles representing the charted ellipses will be π cm^2. Manifestly, the intrinsic properties of the color twofold will thus remain unaffected by our choice of the scale of its model.

We may now turn to the actual evaluation of the curvature K at various places of the color triangle.

The expression for its first part, K_1, may be left as it stands, but that for its more important part K_2 can be conveniently modified as follows:

Let Δa be the increment of a in passing orthogonally (on the chart, Fig. 4) from one a line to the next a line, no matter in which of the two senses.† Then, approximately,

$$(\partial/\partial\eta)(1/a)=(1/\beta)\Delta(1/a),$$

so that

$$\beta(\partial/\partial\eta)(1/a)=\Delta(1/a).$$

By the same token,

$$(\partial/\partial\eta)[\beta(\partial/\partial\eta)(1/a)]=(\partial/\partial\eta)\Delta(1/a)$$
$$=(1/\beta)\Delta^2(1/a).$$

Hence, ultimately,

$$K_2=-(a/100)\Delta^2(1/a).$$

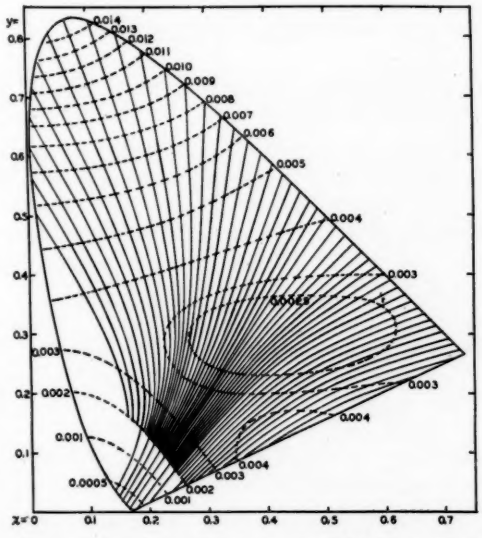

FIG. 4. Directions of major axes (solid lines), lengths (a) of major axes (dotted contours), and lengths (b) of minor axes (one-tenth of separations of solid lines) of noticeability ellipses.

* This is seen also directly from (5) which would then at once become a Euclidean element, $ds^2=dX^2+dY^2$, $X=\int[d\xi/a(\xi)]$, $Y=\int[d\eta/b(\eta)]$.

** So far, a "Nutting-step," to be sure.

† This is immaterial, since $\partial/\partial\eta$ occurs twice; similarly, for $\partial/\partial\xi$.

This is the required working formula. The analogous reduction of K_1 is not feasible, because a similar spacing of the b lines is not practicable.

Let us first explore a few regions where the neighbor a lines are nearly equidistant (on the chart, Fig. 4), i.e., where $\partial\beta/\partial\xi=0$. For such regions, $K_1=0$ and

$$K=-(a/100)\Delta^2(1/a).$$

To compute $\Delta^2(1/a)$ at a point 1, we require $a=a_1$, at that point, and a_2, a_3, the a values at two more points 2, 3 placed on near-by a lines and reached from 1 on a path orthogonal to the a lines. If we take next neighbors, then $\Delta_1(1/a)$ is simply $(1/a_2)-(1/a_1)$,

$$\Delta_2(1/a)=(1/a_3)-(1/a_2),$$

and

$$\Delta^2(1/a)=(1/a_3)-(2/a_2)+(1/a_1).$$

If we take (for technical reasons) next-but-one neighbors, then $\Delta_1(1/a)=\frac{1}{2}[(1/a_2)-(1/a_1)]$, and so on.

It will suffice to describe all details of the computation in a single case. For the remaining similar cases, the final results only will be given.

Starting from

$$x=0.086,\quad y=0.522$$

as our point 1 and taking next-but-one neighbors (to the right) as 2 and 3, we read off from Fig. 4

$$\begin{array}{lll} 1000a_1=6.0 & 1000a_2=6.3 & 1000a_3=6.5, \\ (1/a_1)=167 & (1/a_2)=159 & (1/a_3)=154, \end{array}$$

whence

$$\Delta_1(1/a)=-\frac{8}{2}=-4,\quad \Delta_2(1/a)=-\frac{5}{2}=-2.5.$$

Thus, at the point 1,

$$\Delta^2(1/a)=\tfrac{1}{2}(4-2.5)=0.75$$

and ultimately,

$$K=-4.5\cdot10^{-5},\quad (0.086,\ 0.522)$$

a negative curvature of the order 10^{-5}, apparently not very much, but, as will be shown presently, by no means negligible as to its actual meaning.

In just the same way, we find in the neighborhood of four more places of the color domain, where $\partial\beta/\partial\xi=0$ still holds nearly enough (that is, where K_1/K_2 is quite negligible), the following curvatures:

$$\begin{array}{ll} K=-3.7\cdot10^{-5} & (0.090,\ 0.367), \\ K=-8.5\cdot10^{-5} & (0.190,\ 0.543), \\ K=-4.5\cdot10^{-5} & (0.350,\ 0.539), \\ K=+2.7\cdot10^{-5} & (0.489,\ 0.489). \end{array}$$

Let us now evaluate the curvature at one more place, taking account also of the first term K_1. A glance at Fig. 4 will show that even where the change of β along a considerable stretch of an a line is appreciable, β and $1/\beta$ vary uniformly, i.e., $(\partial/\partial\xi)(1/\beta)$ is very nearly constant. Thus,

$$K_1=-a\beta(\partial a/\partial\xi)\cdot(\partial/\partial\xi)(1/\beta)$$

and, as before,

$$K_2=-(a/100)\Delta^2(1/a).$$

To compute both terms, and thus the complete K, four points are now required: the starting point 1, two points, 2 and 3, arrayed with 1 transversally (as in all preceding cases), and a point 4 on the same a line with 1 and at a goodly distance from it, in order to make $(\partial/\partial\xi)(1/\beta)$ conspicuous.

Keeping this in mind, let us take $x=0.350$, $y=0.467$ as our point 1, the point 2 two curves away from it in the sense of decreasing x, similarly, the point 3 two curves away from 2, and, finally, the point 4 at a distance 0.15 from 1 measured (on the chart) along the a line of 1, which places 4 just on the spectral boundary of the color triangle. For this tetrad of points we have

$$\begin{array}{ll} a_1=0.00425, & a_3=0.00489, \\ a_2=0.00459, & a_4=0.00546, \end{array}$$

and

$$\beta_1=0.1/6=1/60,\quad \beta_4=0.1/4=1/40.$$

Hence,

$$\begin{array}{l} (\partial/\partial\xi)(1/\beta)=(40-60/0.15)=-133, \\ (\partial a/\partial\xi)=0.00121/0.15=0.0081, \end{array}$$

so that

$$K_1=+7.60\cdot10^{-5}.$$

For K_2, we find from the points 1, 2, 3, in the previously explained way,

$$K_2=-4.25\cdot10^{-5}.$$

Thus, ultimately,

$$K = +3.35 \cdot 10^{-5}, \quad (0.350, 0.467)$$

again of the order 10^{-5}.

Let us now try to bring home the significance of all these apparently minute curvatures.

Imagine a small geodesic triangle on the color surface around a place where the curvature has the value K. Let σ be its (true) area. Then the excess Δ of the sum of the angles of the triangle over two right angles will be

$$\Delta = K\sigma,$$

that is, $K\sigma$ radians. It will be recalled that both K and σ are pure numbers; so also is, then, their product.

As we know, the true area of a Nutting ellipse is just the area of a unit circle on the surface. Thus, the excess for a triangle having the area of such an ellipse is

$$\Delta = K\pi = K \cdot 180 \text{ degrees.}$$

E.g., in the neighborhood of $x = 0.19$, $y = 0.54$, where

$$K = -8.5 \cdot 10^{-5},$$
$$\Delta = -0.0153^\circ = -55 \text{ seconds,}$$

a very small defect, no doubt; but so also is the area of the elementary ellipse when compared with the area of the whole color twofold.

The charted area ($\int y dx$) of the region enclosed by the spectrum locus and the straight line joining its extremities is $0.35[x^2]$. The average value of $g^{\frac{1}{2}}$ for this area has been found by MacAdam to be $37 \cdot 10^4$. The total "true area" of the color domain is therefore $37 \times 10^4 \times 0.35 = 13 \times 10^4$. This is more than 40,000 times the true area of one Nutting ellipse. Now consider a geodesic triangle whose true area is $\frac{1}{50}$th of this, i.e.,

$$\sigma = 2600.$$

The excess (or defect) for such a triangle is, therefore,

$$\Delta = 2600K \text{ radians} = K \cdot 1.5 \times 10^5 \text{ degrees.}$$

Thus, e.g., around (0.19, 0.54), where

$$K = -8.5 \cdot 10^{-5},$$
$$\Delta = -1.5 \times 8.5 = -12.6^\circ,$$

i.e., a defect of more than 12 degrees in a triangle forming only $\frac{1}{50}$th of the whole color domain. The departure from flatness will thus be conspicuous even in such a small part of the domain. To realize this the better, notice that the excess in a geodesic triangle covering $\frac{1}{60}$th of the whole surface of any sphere amounts to just 12°. In the neighborhood of (0.19, 0.54), then, the color surface which is here saddle-shaped will differ from a plane about as much as does the earth's surface or any sphere. We have picked out a place of greatest $|K|$. But even at our least curved spot (0.49, 0.49) the excess for such a triangle will amount to some 4°, and elsewhere to −5.5°, and may be much greater in the yet unexplored violet corner of the color triangle.

This will suffice to show that the color surface will differ considerably from the plane or any developable surface.

We can now evaluate the number $n = n(P)$ of "distinct neighbors" of a color P.[4] From the numerical results for K found above, it is manifest that this number will differ from *six* very little. It can be readily calculated how much. In fact, if α be the angle of an equilateral triangle of unit side on the true color surface, with one corner at P, this number is

$$n = n(P) = 2\pi/\alpha.$$

The area of such an elementary triangle may, to all purposes, be attributed its Euclidean value,

$$\sigma = \sqrt{3}/4.$$

(Three hundred thousand, $13 \times 10^4/0.433$, such triangles are enclosed by the spectrum locus.) Its excess (or defect) is $\Delta = K\sigma = (\sqrt{3}/4)$, $K = 0.43K$, whence $\alpha = \frac{1}{3}(\pi + 0.43K)$ and

$$n = 6(1 - 0.14K).$$

Thus, e.g., at the most curved spot (0.19, 0.54) so far found where $K = -8.5 \cdot 10^{-5}$,

$$n = 6(1 + 1.2 \cdot 10^{-5}) = 6.00007,$$

and a little less above or below six elsewhere.

Needless to say, such small departures from six could never be detected by direct observation, on an elementary ellipse or the corresponding *unit* circle, that is. Yet they are of essential importance for the knowledge of the color twofold as a whole and cannot be disregarded. They

[4] L. Silberstein, J. Opt. Soc. Am. **32**, 552–556 (1942).

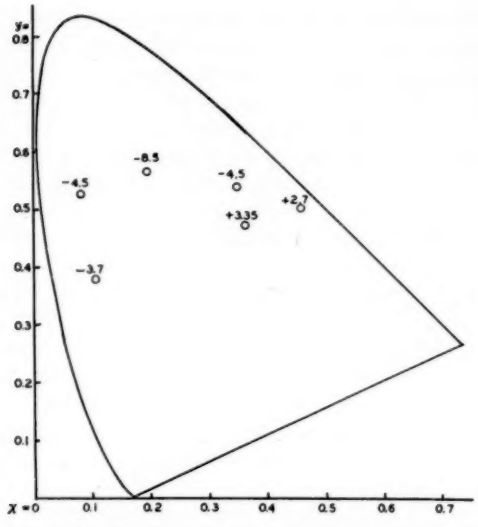

FIG. 5. Distribution of curvatures of true color surface (values indicated should be multiplied by 10^{-5}).

have been determined here, reliably and consistently, from figures many times greater than an elementary ellipse (on the chart) or unit circle (on the surface). Our number of neighbors, differing from each other as much as from the central color, becomes a *practicable* "criterion of representability, etc.," when it is applied to circles whose radii amount to many units. The difference from six being proportional to the square of the radius, that number will then differ considerably from six. Thus, for the triangle treated above and showing a defect of 12.6 degrees, we shall have $\alpha = 55.7°$, and $2\pi/\alpha = 6.5$, that is to say, a cycle of 13 colors in a double tour around the central color.

In fine, the curvatures hitherto found, all of the order 10^{-5} to 10^{-4}, are far from being negligible. Their apparent smallness is merely due to MacAdam's choice of such a small unit of "distance," *viz.*, that of a just perceptible chromaticity difference ($ds = 1$). He had a good reason for this choice, for that distance is certainly a natural unit. If we agreed to set that distance equal to 0.01, all our K values would become 10^4 times greater, and thus $K = -0.85$ at (0.19, 0.54), and so on. However, we prefer the (visually) natural unit. At any rate, whatever the choice of the unit, the true color surface will differ from a plane about as much as does a sphere.

Returning to the handful of curvatures K so far evaluated, we might gather them in a numerical table with x, y as entries. It has seemed better, however, to place these K numbers ($\times 10^5$) on the color chart itself (Fig. 5), wherever they belong. A good many more such numbered spots would, no doubt, be necessary for forming an adequate idea about the distribution of curvature over the color triangle.

JANUARY, 1943 J. O. S. A. VOLUME 33

Adaptation in Color Space*

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(Received October 7, 1942)

1. INTRODUCTION

THE trichromatic system of color specification designates any colored light by three numbers, and thus the color can be represented by a point in a three-dimensional space. The data on which the C.I.E. system is based were obtained with colored lights and a fixed surround but the colors of ordinary experience are not generally seen under the specialized conditions of a constant surround, and their appearance depends on everything in the field of view. For example, the trichromatic system is quite incapable of showing that a bright orange light with dark surround becomes brown when a bright white surround is used.

* Presented at the Summer Meeting of the Optical Society of America at Cambridge, Massachusetts, July 22, 1942.

The artist usually says that the trouble with the trichromatic system is that it is based on experiments with colored lights. The true difficulty, however, is not in the kind of colors used but in the fact that the trichromatic system ignores adaptation.

The purpose of this paper is to inquire into the possibility of introducing the adaptation of the eye into the color specification system. The result can be represented by the introduction of a 6-space instead of the customary 3-space. But it is more convenient to effect the representation by means of a univalent tensor in the 3-space. The new representation allows a more complete specification of color and lays the basis for a scientific treatment of color discrimination and color harmony.

2. THE OSTWALD SCALE

An example of the difficulty caused by neglecting the surround is given by the gray scale of Wilhelm Ostwald.[1] This scale consists of a series of grays ranging from white to black. Ostwald assumed that the grays would appear equally spaced if the reflection factors were arranged according to a logarithmic scale. Examination of his grays, however, as they are mounted on a white background in his book, shows that they are anything but evenly spaced. A similar set of grays with reflection factors arranged logarithmically is shown in Fig. 1. The three darkest grays appear almost identical, while there seem to be large gaps near the white end of the scale. Similar scales are used throughout the Ostwald color solid, and thus the whole system of color harmony as developed by Ostwald[1] and Birren[2] is on an insecure foundation.

Ostwald's idea of using the Fechner law is completely erroneous. The question still remains as to whether some other fixed arrangement of grays might appear equally spaced under all circumstances. Such a possibility seems very remote, for it will be found that a change of the background will distort the relations among the samples. The only solution of the difficulty seems to be in the introduction of a radically different system such as that proposed in the present paper.

3. ADAPTATION OF THE EYE

In the augmented system of color specification introduced in this paper, the state of adaptation of the eye is taken into account. It should be realized that the new system continues to specify stimuli only, not sensations.

The fovea adapts itself to a value of helios which will be called H_A, the adapting helios. Ordinarily the fovea is not uniformly illuminated; but because of the rapid movements of the eyes and the comparatively slow changes in the adaptation process, the adaptation level can be assumed to be constant over this area. The illumination of the outer parts of the retina also affects the foveal adaptation, either by scattering of light in the media of the eye or by action of the transverse neurons of the retina.

Consider first the simplest possible case in which everything is uniform in the field of view. Evidently the eye will adapt itself to the helios of the field. Another simple case is that in which everything is uniform except for a single concentrated source of white light. Numerous experiments[3] have been made showing that the adapting value in this special case is

$$H_A = kD_g\theta^{-\frac{1}{2}}, \tag{1}$$

where k is a constant which is determined experimentally and D_g is the flux density produced at the eye, by the light source, on a plane perpendicular to the line of sight. The angle between the line of sight and the source is designated as θ.

If now the single source is replaced by a continuous distribution $H(\theta, \varphi)$ in the surround, the adapting value becomes

$$H_A = \frac{k}{\pi}\int\int_{\Omega} H(\theta,\varphi)\theta^{-\frac{1}{2}}\sin\theta\cos\theta\, d\theta\, d\varphi, \tag{2}$$

FIG. 1. The gray scale of Ostwald.

[1] W. Ostwald, *Farbkunde* (S. Hirzel, Leipzig, 1923). *Color Science* (Winsor and Newton, Ltd., London, 1931).

[2] F. Birren, *Color dimensions* (Crimson Press, Chicago, 1934).

[3] L. L. Holladay, "Fundamentals of glare and visibility," J. Opt. Soc. Am. **12**, 271 (1926). W. S. Stiles, "The effect of glare on the brightness difference threshold," Dept. of Sci. and Ind. Res., London, Illum. Res. No. 8, 1929.

where Ω is the solid angle of the surround. If $H(\theta,\varphi)=\text{const.}=H$, Eq. (2) becomes

$$H_A=H=\frac{kH}{\pi}\int\int_{\Omega}\theta^{-\frac{1}{3}}\sin\theta\cos\theta\,d\theta\,d\varphi. \quad (3)$$

The adapting value depends not only on the helios of the surround but also on the helios of the objects imaged on the fovea. Assuming that the effect of the luminous elements imaged on the fovea is independent of θ,

$$H_A=cH_{(\text{fovea})}$$

$$+\frac{k}{\pi}\int\int_{\Omega}H(\theta,\varphi)\theta^{-\frac{1}{3}}\sin\theta\cos\theta\,d\theta\,d\varphi. \quad (4)$$

The foregoing treatment is on the basis of white light, as are the experimental results on which the method is founded. Evidently, however, an extension is easily made to colored lights by replacing Eq. (2) by three similar equations, according to the trichromatic theory. Thus,

$$H_{A_i}=\frac{k_i}{\pi}\int\int_{\Omega}H_i(\theta,\varphi)\theta^{-f_i}\sin\theta\cos\theta\,d\theta\,d\varphi,$$

$$i=1,\,2,\,3. \quad (5)$$

The constants k_i and f_i can be obtained experimentally for a given set of primaries. Thus the state of foveal adaptation can be calculated for any given visual field or it can be obtained experimentally.

The foregoing paragraphs have been introduced to clarify the notion of the adapting value and to give a method of determining it precisely. The general conclusions and methods of this paper, however, hold irrespective of the exact details connected with the determination of the adapting value.

4. POSTULATES

The ordinary color space is a three-dimensional affine space. Any color can be represented by a point y^k $(k=1,2,3)$, Fig. 2. Similarly, the trichromatic adapting value[4] can be represented by the point x^k. Both points specify stimuli, not sensation.

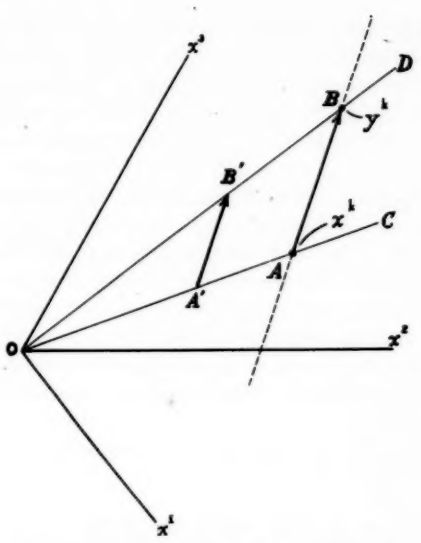

FIG. 2. Geometric representation of composite stimuli.

These six numbers give a six-dimensional specification of the foveal stimulus, including the effect of adaptation. Such a color specification may be used, though there is advantage in reducing the number of independent variables from six to three. This desideratum is accomplished by introducing a new concept, the *composite stimulus*, which is defined by x^k and y^k, subject to the following postulates:

Postulate I. A composite stimulus is represented geometrically by a directed line segment from x^k to y^k. The order of x^k and y^k cannot be interchanged without altering the composite stimulus, except in the trivial case that x^k and y^k coincide.

Postulate II. The necessary and sufficient condition for the equality of two composite stimuli is that

(a) the two line segments are parallel and have the same polarization,[5] and

(b) the affine lengths of the two segments are directly proportional to the respective values of adapting helios, the same proportionality constant being used in both cases.

[4] The present treatment is limited throughout to a single color patch, sufficiently small so that its image lies completely within the fovea. All patches subtend the same visual angle. The point y^k always represents the patch, while x^k represents the visual adaptation.

[5] The term *polarization* is often referred to as "sense." Two parallel vectors may have equal or opposite polarizations depending on the order in which their end points are taken.

According to these postulates, the directed line segment from x^k to y^k, Fig. 2, is equivalent to any other line segment parallel to AB and terminating at the lines OC and OD. But it is more than this. The vector AB can move parallel to itself, provided its length changes in direct proportion to the helios of the adapting value. All line segments having equality under the foregoing postulates are said to represent the *same composite stimulus*. Note, however, that since no metric has been introduced, the space remains affine. Thus no general relation can be established between *non-parallel* segments.

The question immediately arises as to why the concept of the composite stimulus was introduced and what relation it has, if any, to common experience. The purpose of the postulational approach was to eliminate the confusing questions that are sure to arise if one attempts to talk about sensations. The foregoing treatment is based entirely on stimuli. After having set up the method, however, one is free to inquire as to the significance and reasonableness of the consequences of the postulates.

In Fig. 2, for example, suppose that OC represents the "white line" while OD gives a constant quality of red. Then the directed line segment AB represents a red patch on a neutral background. The segment $A'B'$, which is parallel to AB, represents the *identical composite stimulus*, according to the postulates. The definition seems reasonable, for $A'B'$ could be obtained from AB merely by reducing the illumination on a definite pair of surfaces. Under the new illumination, surfaces would appear essentially the same as under the old illumination.*

Consider an *orange patch on a gray background*, the composite stimulus being represented by a line segment from a point x^k on the white line to y^k, which has the trichromatic coordinates of the particular orange used. The object appears as a bright orange color.

One now inquires as to how the same composite stimulus can be obtained if the patch is a piece of the same gray paper formerly used for the background instead of being orange. The point y^k now has the same trichromatic coordinates as were previously used for the adapting point. The new adapting point x^k moves along the line previously determined by the orange and gray points and takes up a position in the blue. The exact location can be determined by methods given in the next section. In other words, identical composite stimuli are obtained with an orange spot on a gray background and with a gray spot on a suitable blue background. This conclusion is in accordance with the well-known result that a hueless patch appears to take on the hue that is complementary to that of the background.

These two special cases illustrate the connection between the new concept of *composite stimulus* and the familiar qualitative results of everyday color experience. The results are not limited to such special cases but apply over the widest range of conditions, and the points for identical composite stimuli can be calculated in all cases. Two words of caution may be in order: first, the calculated points may lie outside the spectral cone and may thus represent fictitious colors; second, the composite stimulus does not represent sensation, though it has a rough correlation with it.

It should be noted that the colors considered in this paper are "unrelated colors," such as would be obtained by using colored lights or colored patches having no particular psychological associations. Such unrelated colors appear to be the kind appropriate for investigations of color harmony.

5. A NEW COLOR TENSOR

A tensor[6] which specifies the composite color stimulus is

$$p^i=(y^i-x^i)/u_kx^k, \quad i, k\doteq 1, 2, 3, \quad (6)$$

where u_1, u_2, u_3 are the coefficients of the planes of constant helios for the adapting value x^k:

$$u_1x^1+u_2x^2+u_3x^3=H. \quad (7)$$

This tensor is of valence one but is distinct from the ordinary vector in that its magnitude is a function of position.[7] The quantity p^i is a tensor,

* Subject, of course, to the limitations implicit in the C.I.E. spstem.

[6] The notation, insofar as possible, is in accordance with J. A. Schouten and D. J. Struik, *Einführung in die neueren Methoden der Differentialgeometrie* (Noordhoff, Groningen, 1935). The superscripts i and k are indices, not exponents.

[7] D. E. Spencer, "A tensor interpretation of Study's *Geometrie der Dynamen*," Ph.D. Thesis, M.I.T., 1942.

since it is the quotient of an ordinary vector and a scalar function (the helios of the adapting value) which is invariant under affine transformations. Since p^i changes sign when y^i and x^i are interchanged, the first postulate is satisfied.

The tensor p^i is completely determined by three properties. These are its direction, $p^1 : p^2 : p^3$; its polarization[5] which is the distinction between color patch and adapting value; and its magnitude. All line segments that are parallel and have the same polarization are represented by tensors that are scalar multiples of one another. In general, two such tensors which are parallel and of the same polarization satisfy the condition,

$$({}^{(1)}y^i - {}^{(1)}x^i)/u_k{}^{(1)}x^k = k[({}^{(2)}y^i - {}^{(2)}x^i)/u_k{}^{(2)}x^k], \qquad k \text{ a positive constant.} \quad (8)$$

If k is equal to unity, the two tensors are identical. But under these circumstances Eq. (8) reduces to part (b) of Postulate II.

Suppose that a composite color stimulus p^i is given, as well as an adapting value x^i. The color patch which must be used to provide the composite stimulus has the trichromatic coordinates

$$y^i = x^i + (u_k x^k)p^i. \quad (9)$$

On the other hand, let the color patch y^i be given. It is desired to find the adapting value that must be used. This adapting value is obtained by solving the following three simultaneous linear equations in x^i:

$$(u_k x^k)p^i + x^i = y^i. \quad (10)$$

If two color patches y^i and z^i are added while the adapting value x^i is kept constant, the composite stimulus has the equation

$$p^i = (y^i + z^i - x^i)/u_k x^k, \quad (11)$$

which is not equal to the sum of the two composite stimuli. Composite stimuli can be added only when both color patches and adapting values are added.

If a color patch is multiplied by a scalar,

$$p^i = (ky^i - x^i)/u_k x^k. \quad (12)$$

The line segment representing the new composite color stimulus is in general different in direction and hence cannot be compared with the old one in magnitude. It is only when x^i and y^i are on a line of constant quality, so that $x^i = cy^i$, that the new composite stimulus has the same direction. The equation for this composite stimulus is

$$p^i = [(k-c)y^i]/u_k x^k. \quad (13)$$

Thus the ratio of these composite stimuli is

$$R = (k-c)/(1-c). \quad (14)$$

The foregoing equations apply to any trichromatic specification of the individual stimuli. In the special case of the C.I.E. system, they assume a particularly simple form. It is well known that in the C.I.E. system

$$u_1 = 0, \quad u_2 = 1, \quad u_3 = 0. \quad (15)$$

Thus Eq. (16) becomes

$$p^i = (y^i - x^i)/x^2, \quad i = 1, 2, 3. \quad (16)$$

The component p^2 also takes on additional significance for

$$p^2 = \frac{y^2 - x^2}{x^2} = [H(y^i) - H(x^i)]/H(x^i). \quad (17)$$

Therefore in the C.I.E. system p^2 is the difference in helios of color patch and surround expressed as a fraction of the helios of the adapting value. This quantity has often been called the *contrast*.

6. EXAMPLES

A few numerical examples will now be given to illustrate some of the possibilities of the new method of color specification.

(I) For instance, the C.I.E. specification of a certain orange upholstery material[8] is

$$y^1 = 0.2764, \quad y^2 = 0.1918. \quad y^3 = 0.0596,$$

when Illuminant C is used. A commercially available gray background material is specified by

$$x^1 = 0.1602, \quad x^2 = 0.1644, \quad x^3 = 0.1866.$$

It will be assumed that the background is sufficiently large and the orange spot is sufficiently small so that the adaptation can be specified by the foregoing numbers. Then, from Eq. (6),

[8] Material No. 587 from Parry Moon, "Colors of furniture," J. Opt. Soc. Am. **32**, 293 (1942).

the composite stimulus is determined by three numbers:

$$p^1=\frac{0.1162}{0.1644}=0.7068,\quad p^2=\frac{0.0274}{0.1644}=0.1667,$$

$$p^3=-\frac{0.1270}{0.1644}=-0.7725.$$

If the same orange patch is now placed on a white background so that the adaptation is specified by the coordinates,

$$x^1=0.7811,\quad x^2=0.8039,\quad x^3=0.8961,$$

then the composite stimulus is

$$p^1=-\frac{0.5047}{0.8039}=-0.6278,$$

$$p^2=-\frac{0.6121}{0.8039}=-0.7614,$$

$$p^3=-\frac{0.8365}{0.8039}=-1.0406.$$

Thus the composite stimuli are completely different in the two cases, though exactly the same color sample is used. This distinction is ignored by the ordinary trichromatic system.

(II) Given an orange spot on a gray background:

$$p^1=0.7068,\quad p^2=0.1667,\quad p^3=-0.7725.$$

What state of adaptation must be used to obtain the same composite stimulus when a gray spot is used instead of the orange one?

From Eq. (10),

$$x^2p^2+x^2=y^2$$
$$x^2p^1+x^1=y^1$$
$$x^2p^3+x^3=y^3.$$

If the gray patch is represented by

$$y^1=0.1602,\quad y^2=0.1644,\quad y^3=0.1866,$$

the first of these three equations gives

$$x^2=0.1409,$$

while substitution in the other equations results in

$$x^1=0.0606,\quad x^3=0.2954.$$

These three numbers represent the C.I.E. specification (X, Y, Z) of the adaptation and show that the background must be blue to make the gray patch look orange. The standard two-dimensional specification is

$$x=0.1220,\quad y=0.2836.$$

(III) Given a gray patch on a green background:

$$y^1=0.1953,\quad y^2=0.2010,\quad y^3=0.2240;$$
$$x^1=0.1261,\quad x^2=0.1748,\quad x^3=0.1611.$$

What is the trichromatic specification of a color which, when used with a white background, will provide the same composite stimulus?

Application of Eq. (6) gives the specification:

$$p^1=0.3959,\quad p^2=0.1499,\quad p^3=0.3598.$$

This same composite stimulus is to be obtained with a new adaptation:

$$x^1=0.7811,\quad x^2=0.8039,\quad x^3=0.8961.$$

The trichromatic coordinates of the new color patch are obtained from Eq. (9), or

$$y^1=0.7811+(0.8039)(0.3959)=1.0994=X$$
$$y^2=0.8039+(0.8039)(0.1499)=0.9244=Y$$
$$y^3=0.8961+(0.8039)(0.3598)=1.1853=Z.$$

The position in the color 2-space is designated by

$$x=0.3426,\quad y=0.2881,$$

which represents an unsaturated purple. This conclusion is in accordance with the familiar fact that a neutral spot will appear to take on the hue complementary to that of the background.

(IV) Another question that often arises is how the appearance of a combination of colored materials will change when the illumination is changed from daylight to artificial light. A certain blue patch on a gray background, when lighted by Illuminant C, is specified by

$$y^1=0.1826,\quad y^2=0.1837,\quad y^3=0.4756$$
$$x^1=0.1602,\quad x^2=0.1644,\quad x^3=0.1866$$
$$p^1=0.1363,\quad p^2=0.1174,\quad p^3=1.7579.$$

The corresponding values for Illuminant A are

$$y^1=\ 0.1502,\quad y^2=\ 0.1595,\quad y^3=\ 0.1394$$
$$x^1=\ 0.1809,\quad x^2=\ 0.1676,\quad x^3=\ 0.0563$$
$$p^1=-0.1832,\quad p^2=-0.0483,\quad p^3=+0.4958.$$

The composite stimuli are completely different in the two cases, indicating that the appearance will be different under artificial light and daylight. To obtain an idea of the amount of this difference, one may inquire as to the trichromatic coordinates required for the blue under Illuminant C so that its composite stimulus would be

$$p^1=-0.1832, \quad p^2=-0.0483, \quad p^4=+0.4958.$$

The results are

$$y^1=0.1602-(0.1644)(0.1832)=0.1301$$
$$y^2=0.1644-(0.1644)(0.0483)=0.1565$$
$$y^3=0.1866+(0.1644)(0.4958)=0.2681.$$

Comparison with the original values of y^k for Illuminant C indicates that the blue will appear very dark when illuminated by light from incandescent lamps. In the C.I.E. 2-space, the coordinates are $x=0.2345$. $y=0.2821$ instead of the original values of $x=0.2170$, $y=0.2182$.

As another example of the same kind, consider a chartreuse sample on a gray background. For Illuminant C and the same adaptations as used previously,

$$y^1=0.3698, \quad y^2=0.4380, \quad y^3=0.1968$$
$$p^1=1.2749, \quad p^2=1.6642, \quad p^3=0.0620.$$

For Illuminant A,

$$y^1=0.4460, \quad y^2=0.4413, \quad y^3=0.0637$$
$$p^1=1.5817, \quad p^2=1.6331, \quad p^3=0.0442.$$

These values are not far from those for the composite stimulus obtained with Illuminant C, which indicates that the effect of the illuminant is much less marked than with the blue sample.

7. CORRELATION WITH SENSATION

As stated previously, no exact correlation is possible between composite stimulus and sensation because of the intrinsic inaccuracy of any experimental data on sensation. Nevertheless, it is interesting to compare composite stimuli with experimental results. The best data of this kind appear to be those of Helson.[9] He took a set of neutral gray papers having reflection factors from 0.80 to 0.03. These samples were spread out on a shelf and were viewed under chromatic illuminations. Neutral backgrounds were employed, having reflection factors of 0.80, 0.22, and 0.03. The observers, who had previously studied the *Munsell Book of Color*,[10] were adapted to one of the chromatic illuminations and were then asked to attach Munsell specifications to the appearances of the neutral samples.

The general conclusions of Helson were as follows:

(1) If the reflection factor of a sample is greater than the adapting reflection factor, the sample takes on the hue of the illuminant.

(2) If the reflection factor of the sample is less than the adapting reflection factor, the sample appears to have a hue complementary to that of the illuminant.

(3) If the reflection factors of background and sample are equal, the sample appears achromatic.

A little thought will show that these conclusions are in complete agreement with the predictions of the composite stimulus method. The correlation is shown in greater detail by Table I, which contains the experimental results of Helson, also the Munsell specifications based on the method enunciated in this paper. The calculated trichromatic coefficients are in some cases outside the Munsell color solid, and certain assumptions were made regarding the way in which the observer attached Munsell numbers under such conditions. It was assumed that the brightest of the samples in the field of view was associated with the Munsell lightness specification of 9.0, while the most saturated sample had a saturation of 8.0. The Munsell hues were obtained by comparing the dominant wave-length of the computed composite stimulus with the known dominant wave-lengths for the Munsell paper.[11] The values of adaptation used in the computation of p^i were made on the assumption that all the samples and the neutral background were in the field of view. The empirical formula,

$$A'=0.04561A_0+0.1680A \qquad (18)$$

was employed. The quantities A', A_0, and A are adaptation reflection factor, background reflection factor, and arithmetic mean of reflection factor of samples.

[9] H. Helson, "Fundamental problems in color vision," J. Exp. Psychol. **23**, 439 (1938).

[10] *Munsell Book of Color* (Munsell Color Co., Inc., Baltimore, 1929).

[11] "The Munsell color system," J. Opt. Soc. Am. **30**, 574 (1940).

TABLE I. Comparison of experimental and theoretical values. ρ_s = reflection factor of sample, ρ_b = reflection factor of background.

	$\rho_b = 0.80$		$\rho_b = 0.22$		$\rho_b = 0.03$	
ρ_s	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
			Red illuminant			
0.80	*R* 9/5	*R* 9/5	*R* 8.5/7	*R* 9/5	*R* 7/7	*R* 9/8
0.39	*A* 6/0	*A* 7/0	*bR* 6/3	*R* 7/4	*R* 6/7	*R* 7/7
0.22	*B* 5/3	*BG* 6/3	*RB* 5.5/2	*R* 5/3	*bR* 4,5/4.5	*R* 5/5
0.13	*B* 5/5	*BG* 5/5	*A* 5/0	*A* 5–0	*bR* 4/4	*R* 4/4
0.03	*BG* 3/7	*BG* 3/8	*BG* 1/8	*BG* 1/8	*A* 0/0	*A* 0/0
			Green illuminant			
0.80	*YG* 9/1	*YG* 9/1	*YG* 8/6	*YG* 9/6	*YG* 9/7	*YG* 9/8
0.39	*A* 7/0	*A* 8/0	*YG* 6/3	*YG* 7/1	*YG* 6/5	*YG* 7/7
0.22	*BR* 7/1	*RB* 6/1	*A* 5/0	*A* 6/0	*YG* 4.5/5	*YG* 6/6
0.13	*BR* 6/3.5	*RB* 4/5	*A* 4/0	*RB* 6/1	*YG* 3.5/4	*YG* 4/4
0.03	*BR* 3/8	*RB* 2/8	*RB* 2/8	*RB* 2/8	*A* 0.5/0	*A* 2/0
			Blue illuminant			
0.80	*B* 9/1	*B* 9/1	*B* 8/8	*B* 9/8	*B* 7/6	*B* 9/6
0.39	*A* 6/0	*A* 8/0	*B* 6/5	*B* 7/5	*B* 5/5	*B* 7/5
0.22	*Y* 5/1	*Y* 6/1	*rB* 5/1	*B* 6/4	*rB* 4/4	*B* 5/4
0.13	*Y* 4/2	*Y* 4/4	*A* 3.5/0	*A* 6/0	*rB* 3.5/4	*B* 3/3
0.03	*Y* 2/6	*Y* 2/8	*RY* 1/5.5	*Y* 2/6	*A* 0.5/0	*Y* 2/8
			Yellow illuminant			
0.80	*gY* 9/1	*Y* 9/1	*Y* 8/7	*Y* 9/5	*Y* 9/7	*Y* 9/8
0.39	*A* 7/0	*A* 8/0	*Y* 6.5/3	*Y* 7/3	*Y* 6/4	*Y* 7/7
0.22	*RB* 6/2	*B* 6/2	*A* 6/0	*Y* 5/1	*Y* 5/1	*Y* 5/4
0.13	*RB* 6/4	*B* 4/5	*A* 5/0	*A* 5/0	*Y* 5/1	*Y* 4/2
0.03	*RB* 2/8	*B* 2/8	*B* 1/6	*B* 2/8	*RB* 1/3	*B* 2/2

Table I indicates a good correlation between the experimental results of Helson and the values calculated by the component stimulus method. Most of the values check within one or two Munsell steps. This would, of course, be a large error in the case of direct comparison of color samples. But it must be remembered that in the Helson experiments the observer compares a sensation with the remembrance of a previous sensation which may have been experienced days or weeks before. Obviously, the precision of the experimental data of this type is of a different order of magnitude from that obtained from physical measurements and it is doubtful if a better check between sensation and the composite stimulus could be expected.[12]

8. CONCLUSIONS

The trichromatic method of color specification is firmly established and has proved to be of great practical value. The present paper considers an extension of the trichromatic method to include the effect of adaptation of the eye. By the introduction of a new concept, the *composite stimulus*, the investigator is able to represent a color sample and its background by means of a single new tensor p^k. A variety of interesting color problems can be handled by the use of this tensor, which fortunately is very simple and which leads to calculations no more complicated than those usually associated with the trichromatic system.

The composite stimulus is a rigorously exact concept based on two postulates. It refers to stimuli, not sensations, and it is correct by definition. Thus there can be no question of experimental verification of the calculated values of p^k. The only question is in regard to the relation between the quantitative specification of the stimulus and the designation of the sensation. But it is meaningless to inquire whether there exists an exact correlation between the composite stimulus and the resulting sensation. It is a truism that sensation cannot be measured, in the sense that physical quantities are measured. The only way in which any correlation can be obtained between sensation and composite stimulus is by highly inexact methods. A correlation between the composite stimulus and the experimental data of Helson has been shown. Thus the new tensor p^k provides for the first time a quantitative answer to many color questions, and this answer appears to be in agreement with familiar color facts, insofar as they are amenable to specification.

The new color tensor has its immediate application in the specification of color stimuli and the comparison of color samples with the widest range of backgrounds. Further extensions of the method, such as the introduction of a metric, will probably lead to a more adequate discussion of color discrimination and a better basis for future work on color harmony.

[12] D. B. Judd, "Hue saturation and lightness of surface colors with chromatic illumination," J. Opt. Soc. Am. **30**, 2 (1940).

Specification of Small Chromaticity Differences*†

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IN a previous article data were given specifying sets of equiluminous colors which have been observed to be equally noticeably different from each of twenty-five representative colors.[1] These results were represented adequately by ellipses drawn around the points in the I.C.I. chromaticity diagram representing each of the twenty-five fixed colors. In Fig. 48 of reference 1, the ellipses are enlarged ten times radially in comparison with the ellipses representing the observed standard deviations of color matching. The sizes, shapes, and orientations of the axes of these ellipses vary throughout the diagram in a manner which appears to be systematic. These trends encourage the interpolation of ellipses representing colors equally noticeably different from any other fixed colors. Experience has shown that the sizes, shapes, and orientations of intermediate ellipses can be estimated with sufficient accuracy for most practical purposes. Such estimates are, however, not fully satisfying and the construction of the required ellipses is inconvenient. More direct methods of interpolating between the observed data and of expressing the magnitudes of chromaticity differences have therefore been sought.

The fundamental principles of a convenient method for specifying chromaticity differences are found in an article published by Ludwik Silberstein.[2] Dr. Silberstein has generously assisted in the present application of differential geometry to color specification and has suggested many useful relations.

Each of the twenty-five ellipses representing the known standard deviations of color matching can be represented by the equation

$$g_{11}dx^2+2g_{12}dx\,dy+g_{22}dy^2=1. \qquad (1)$$

In this equation, dx is the difference of the x coordinates of the center of the ellipse and any point on the ellipse; dy is the difference of the y coordinates for the same pair of points; and g_{11}, g_{12}, and g_{22} are constants for each ellipse. The values of g_{11}, g_{12}, and g_{22} may be computed from the lengths a and b of the principal semiaxes of each ellipse, and the angle of inclination θ of the major axis to the axis of x coordinates:

$$g_{11}=\cos^2\theta/a^2+\sin^2\theta/b^2, \qquad (2a)$$

$$g_{12}=\sin\theta\cos\theta(1/a^2-1/b^2), \qquad (2b)$$

$$g_{22}=\sin^2\theta/a^2+\cos^2\theta/b^2. \qquad (2c)$$

These coefficients can be determined with greater convenience and accuracy from the length dx_0 of the horizontal radius of the ellipse (for which $dy=0$), the length dy_0 of the vertical radius of the ellipse (for which $dx=0$), and the lengths dp and dq of the radii which are inclined at $\pm45°$ from the horizontal:

$$g_{11}=1/dx_0^2, \qquad (3a)$$

$$2g_{12}=1/dp^2-1/dq^2, \qquad (3b)$$

$$g_{22}=1/dy_0^2. \qquad (3c)$$

The values for g_{11}, g_{12}, and g_{22} differ from one ellipse to another in manners which appear to be systematic. The variations of these coefficients, as functions of position of the central color in the I.C.I. chromaticity diagram are represented within 30 percent by the contour diagrams shown in Figs. 1, 2, and 3.* Each of the numerical values indicated in Figs. 1, 2, and 3 should be multiplied by 10,000. The departures from the computed coefficients were introduced by the smoothing and adjustment of the curves into consistent families. Discrepancies of this magnitude are consistent with the 15 percent uncertainties which are attributed to the observed standard deviations of color matching. The contours, which indicate rather complicated dependence on the loca-

* An abstract of this article appears in the Proceedings of the Twenty-Seventh Annual Meeting of the Optical Society of America, J. Opt. Soc. Am. **32**, 744 (1942).

† Communication No. 886 from the Kodak Research Laboratories.

[1] D. L. MacAdam, "Visual sensitivities to color differences in daylight," J. Opt. Soc. Am. **32**, 247–274 (1942).

[2] L. Silberstein, "Investigations on the intrinsic properties of the color domain," J. Opt. Soc. Am. **28**, 63–85 (1938).

* All of the data employed in the derivation of Figs. 1, 2, and 3 were obtained with a single observer, Mr. Perley G. Nutting, Jr., who is now Lieutenant, U. S. N.

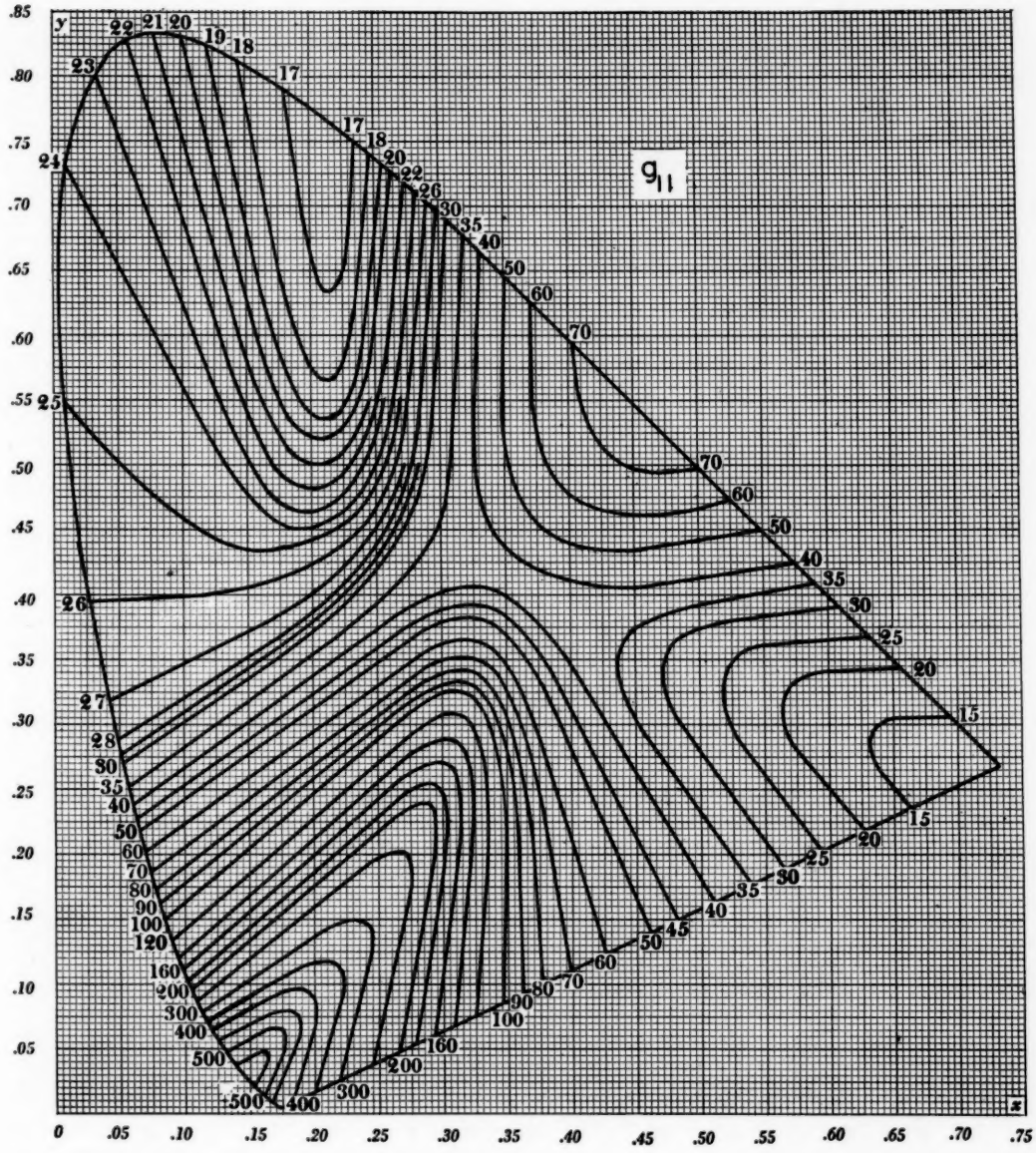

FIG. 1. Values of the coefficient g_{11} (to be multiplied by 10^4) for various locations in the I.C.I. chromaticity diagram.

tion in the chromaticity diagram, are no more complicated than are necessary to represent the observed data within the accuracy of the determinations.

The limited number (25) of observed ellipses, the magnitudes of the experimental uncertainties, and the complicated dependence of the coefficients on chromaticity required the exercise of considerable judgment in the construction of the contour diagrams. Consequently, other justifiable systems of contours might be drawn for equally accurate representation of the coefficients of the observed ellipses. The author believes, however, that no other equally adequate representation of

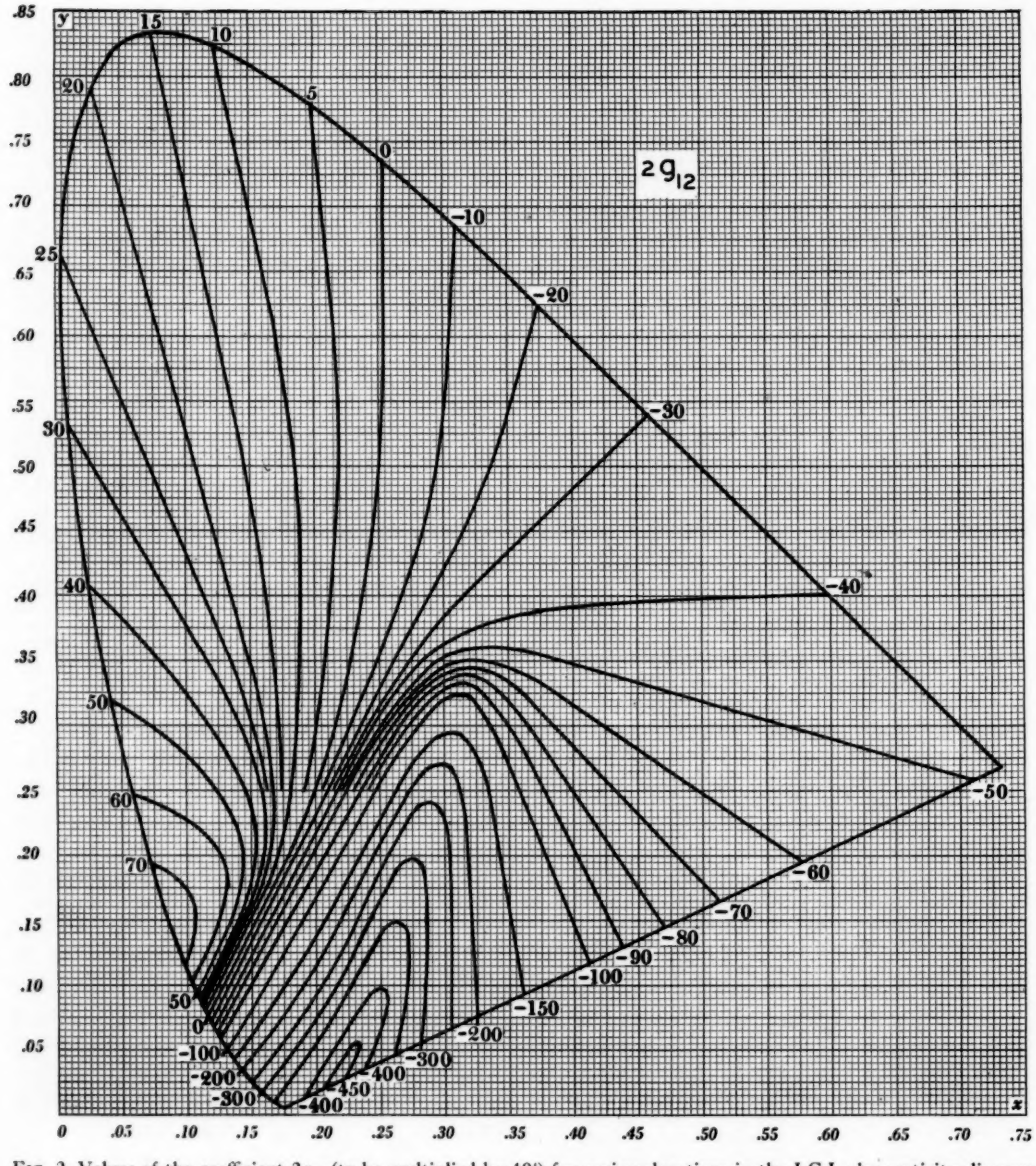

FIG. 2. Values of the coefficient $2g_{12}$ (to be multiplied by 10^4) for various locations in the I.C.I. chromaticity diagram.

the data can yield significantly different interpolated values of the coefficients and that the trends indicated by these contour diagrams are genuine. Thus, although more extensive data would be preferable for the construction of such diagrams, the tentative distributions of values of the coefficients shown in Figs. 1, 2, and 3 are adequate representations of the data available at present. Sufficiently extensive data to assure a more correct representation of such distributions do not appear likely to become available in the near future. In the interim, Figs. 1, 2, and 3 may prove useful in the specification of color differences.

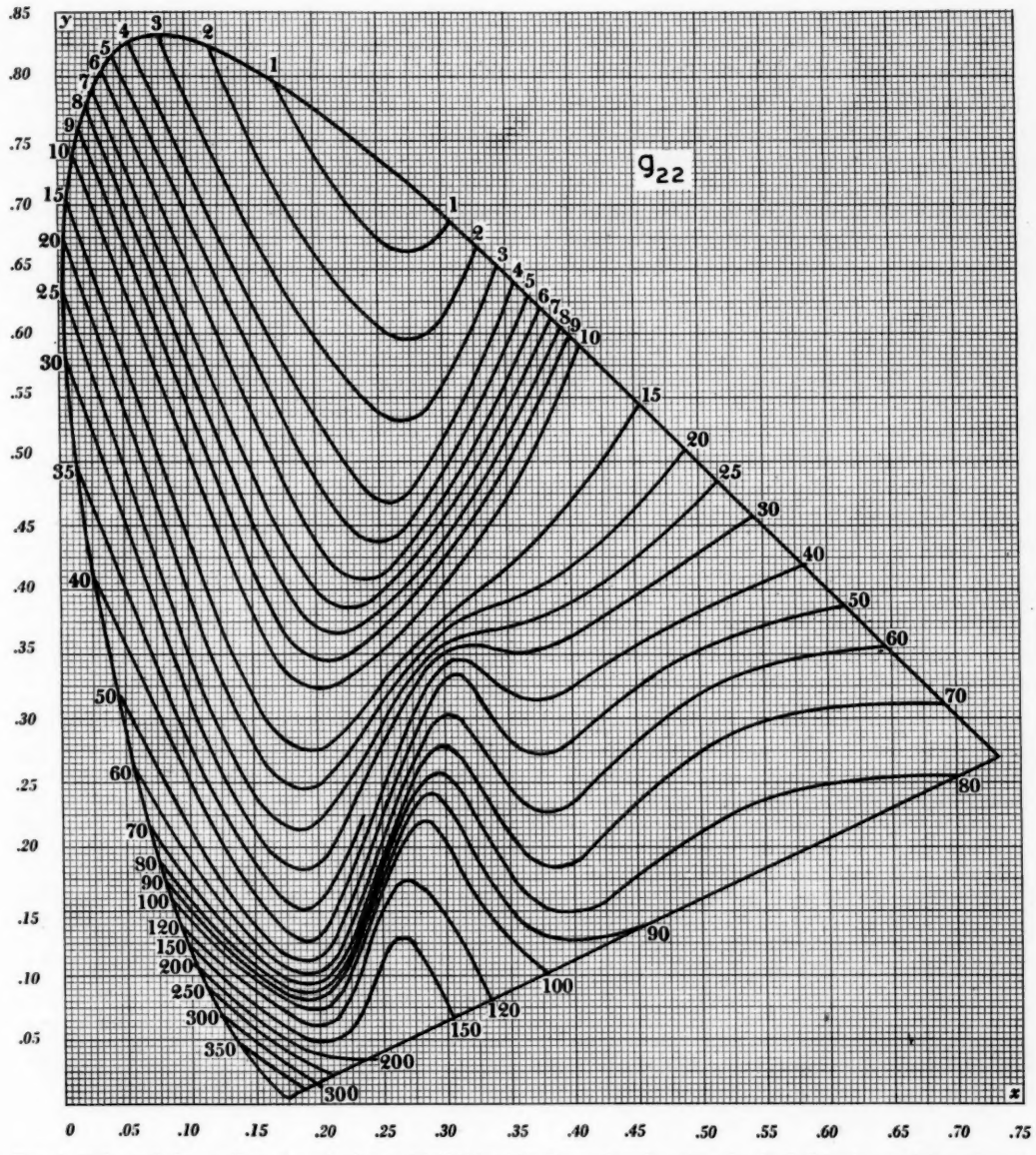

FIG. 3. Values of the coefficient g_{22} (to be multiplied by 10^4) for various locations in the I.C.I. chromaticity diagram.

The orientation θ and lengths a and b of the principal semi-axes of the ellipse, representing the standard deviations of chromaticity matching for all directions of departure from any fixed chromaticity, may be derived from the values of the coefficients g_{11}, g_{12}, g_{22} indicated for that central color in Figs. 1, 2, and 3. Attention should be called to the fact that values of $2g_{12}$ are indicated in Fig. 2, and that when values of g_{12} are employed in the following equations, and elsewhere, the values indicated by Fig. 2 should be divided by two.

$$\tan 2\theta = 2g_{12}/(g_{11}-g_{22}) \qquad (4a)$$

$\theta < 90°$ when $g_{12} < 0$, $\theta > 90°$ when $g_{12} > 0$,

$$1/a^2 = g_{22} + g_{12} \cot \theta, \tag{4b}$$

$$1/b^2 = g_{11} - g_{12} \cot \theta. \tag{4c}$$

The ellipse may be constructed from these values, but the necessity of constructing such ellipses will be almost completely eliminated by the methods which follow.

The ratio of any chromaticity difference to the corresponding standard deviation of color matching will be denoted by ds. Then

$$ds^2 = g_{11}dx^2 + 2g_{12}dx\,dy + g_{22}dy^2. \tag{5}$$

In this definition, dx is the difference of the x coordinates representing the two chromaticities whose difference is to be specified, dy is the difference of the y coordinates representing the chromaticities taken in the same order, and the coefficients g_{11}, $2g_{12}$, and g_{22} are indicated by the contour diagrams for the region intermediate between the two chromaticities. For example, the two yellow (D) lines in the spectrum of sodium (589.00 and 589.59 millimicrons) are represented by the points ($x=0.5693$, $y=0.4300$) and ($x=0.5728$, $y=0.4265$), respectively. In this case, $dx=0.0035$ and $dy=-0.0035$. From Fig. 1, $g_{11}=42\times10^4$ for this region. From Fig. 2, $2g_{12}=-38\times10^4$, and from Fig. 3, $g_{22}=37\times10^4$. Therefore,

$$ds^2 = 42\times0.1225 + 38\times0.1225 + 37\times0.1225 = 14.35.$$

$$ds = 3.8,$$

indicating that the D lines of the sodium spectrum exhibit a difference of chromaticity 3.8 times as great as the standard deviations of color matching by Mr. Nutting. A second example will indicate the general usefulness of this method of calculation. The chromaticity of the light from a blackbody ($c_2=1.436$ cm degree) at a temperature of 4000°K is represented by the point ($x=0.3799$, $y=0.3764$), and that of a blackbody at 3900°K is represented by ($x=0.3844$, $y=0.3793$). In this case, $dx=0.0045$ and $dy=0.0029$. The coefficients indicated for this region in Figs. 1, 2, and 3 are: $g_{11}=39\times10^4$, $2g_{12}=-43\times10^4$, and $g_{22}=25\times10^4$. Therefore,

$$ds^2 = 39\times0.45^2 - 43\times0.45\times0.29 + 25\times0.29^2 = 4.44,$$

$$ds = 2.11,$$

indicating that the difference of 100°K of color temperature near 4000°K is slightly more than twice as noticeable as Mr. Nutting's standard deviation of color matching in the same chromaticity region, and for the same kind of color variation. Furthermore, this result indicates that a difference of 100°K from a color temperature of 4000°K corresponds to about half as great a chromaticity difference as that exhibited by the pair of D lines in the spectrum of sodium. Such specifications and intercomparisons may be investigated with great facility by using Eq. (5) and the contour diagrams.

The theorems and formulas of differential geometry may be applied directly to the study of chromaticity differences expressed in terms of Eq. (5). Such studies have been suggested and outlined by Helmholtz,[3] Schrödinger,[4] Sinden,[5] and Silberstein,[2] but adequate data for such purposes have not previously been available. In a forthcoming article, Dr. Silberstein will discuss the intrinsic properties of the color domain as deduced from the data presented in Figs. 1, 2, and 3. The present paper is concerned only with the use of immediately applicable formulas suggested by Dr. Silberstein's investigations.

It is frequently necessary to choose from a continuous series of chromaticities (which are represented in the I.C.I. diagram by a smooth locus) the chromaticity which is least different from a fixed chromaticity near but not on that locus. This problem is most familiar in connection with the specification of light sources in terms of color temperature when their chromaticities are nearly but not exactly identical with the light from a blackbody at some temperature. For example, a light source having a chromaticity specified by ($x=0.3840$, $y=0.3840$) is represented by a point near but not coincident with the blackbody locus in the neighborhood of 4000°K. The chromaticity of the most nearly similar blackbody may be determined by constructing the noticeability ellipse around the point representing the source and drawing the tangent to this ellipse,

[3] H. V. Helmholtz, "Kürzeste Linien im Farbensystem," Sitz. Akad. Wiss. Berlin, Phys. Math. 1071–1083 (1891); Wiss. Abhandl. **3**, 460–475 (1895).

[4] Erwin Schrödinger, "Grundlinien einer Theorie der Farbenmetrik im Tagessehen," Ann. d. Physik **63**, 397–426, 427–456, 481–520 (1920).

[5] R. H. Sinden, "A further search for the ideal color system," J. Opt. Soc. Am. **27**, 124–131 (1937); **28**, 339–347 (1938).

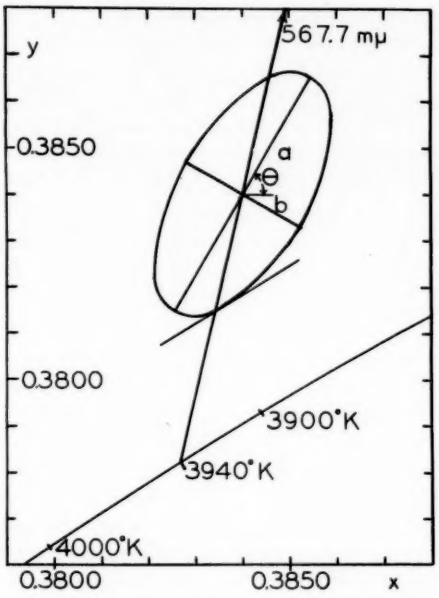

FIG. 4. Construction for graphical determination of nearest color temperature for source not exactly matching any Planckian radiator.

parallel to the nearest portion of the blackbody locus. The intersection of the blackbody locus with the straight line drawn through the center of the ellipse and the point of contact of the tangent represents the chromaticity of the most nearly similar blackbody. This construction is indicated in Fig. 4. In the neighborhood of the point representing the source, the coefficients are $g_{11}=39\times10^4$, $g_{12}=-21\times10^4$, $g_{22}=24\times10^4$. When these values are substituted in Eq. (4a),

$$\tan 2\theta=-42/(39-24)=-2.8$$

and the inclination θ of the major axis of the ellipse from the horizontal x axis is 54.8°. The cotangent of this angle is 0.5765, and when this value and the above coefficients are substituted in Eqs. (4b) and (4c):

$$1/a^2=(24-21\times0.5765)\times10^4 =12\times10^4, \quad a=0.00288;$$
$$1/b^2=(39+21\times0.5765)\times10^4 =51\times10^4, \quad b=0.00140.$$

The ellipse in Fig. 4 has been constructed from these values. The elaborate construction just described is fortunately unnecessary for the determination of nearest color temperature and similar problems.

A simple formula for the slope m' of the line joining the point representing any chromaticity with the most nearly similar chromaticity selected from a continuous series such as the blackbody colors can be derived from the general expression for orthogonality of line elements in Riemannian geometry.[2] If g_{11}, g_{12}, g_{22} are the values of the coefficients in the region between the fixed point and the locus representing the series from which the most nearly similar chromaticity is to be selected, and if m is the slope of that locus in the neighborhood of the fixed point, then

$$m'=-(g_{11}+g_{12}m)/(g_{12}+g_{22}m). \qquad (6)$$

When it is desirable for the avoidance of rejection errors, the reciprocal of either of the slopes may be employed by using the appropriate and easily derived modification of this formula. In the example already discussed, the slope of the blackbody locus in the neighborhood of 4000°K is $m=dy/dx=0.0029/0.0045=0.64$. Therefore, the slope of the line from the fixed point to the point representing the most nearly similar blackbody chromaticity is

$$m'=-(39-21\times0.64)/(-21+24\times0.64) =26/6=4.3.$$

This line is easily constructed, and its intersection ($x=0.3826$, $y=0.3782$) with the blackbody locus corresponds to a color temperature of 3940°K. The kind of chromaticity difference between the source and the most nearly similar blackbody may be specified in terms of the conjunctive wave-length, which is the wave-length corresponding to the intersection of the spectrum locus and the line just constructed through the point representing the source. In the present example, the conjunctive wave-length is 567.7 mμ. The magnitude of the chromaticity difference between the source and a blackbody at 3940°K may be computed by use of Eq. (5) in the same manner as in previous examples. In this case, $dx=0.0014$, $dy=0.0058$; therefore

$$ds^2=39\times0.02-42\times0.081 +24\times0.337=5.48, \quad ds=2.34.$$

Consequently, the point ($x=0.3840$, $y=0.3840$) represents a source having a color temperature of

3940°K, differing visually from a blackbody at that temperature in the same manner as would be obtained by admixture of a small amount of spectrum energy having a wave-length of 567.7 millimicrons, the magnitude of that difference being as noticeable as a difference of about 110°K in color temperature in the same region.

The selection of the closest match to a specified chromaticity, from *any* series represented by a smooth locus in the same neighborhood, can be accomplished by use of the method just illustrated. The kind and degree of residual chromaticity difference may be specified analogously.

It is frequently desirable to represent the chromaticity relationships among a large number of similar samples, one of which may, for example, be a standard to which all of the others are approximations. Such distributions of chromaticities could be represented by plotting the corresponding points in the appropriate section of the standard I.C.I. chromaticity diagram. The proper noticeability ellipse may be determined for that section of the I.C.I. diagram and drawn in the working chart. The ellipse is helpful in interpreting the chromaticity differences charted in this way. The noticeability of the difference between any pair of these chromaticities can be determined as the ratio of the distance in the I.C.I. diagram to the length of the parallel radius of the ellipse. Such constructions and comparisons are not convenient, and some simple representation is, therefore, desirable. The magnitudes of the chromaticity difference between any pair of neighboring colors can be computed from Eq. (5), but such computations become laborious when numerous and the results give no indication of the kind of chromaticity difference. The following graphical method eliminates the necessity for constructing ellipses or evaluating Eqs. (5) or (6).

Every noticeability ellipse may be transformed into a circle of unit radius, if x and y are plotted as oblique coordinates. The angle ω between the axes of x and y necessary to accomplish this is given by

$$\cos \omega = g_{12}/(g_{11}g_{22})^{\frac{1}{2}}. \qquad (7)$$

The scale unit for x, measured parallel to the corresponding axis should be proportional to $(g_{11})^{\frac{1}{2}}$, and the scale unit for y should be proportional to $(g_{22})^{\frac{1}{2}}$. Unit distance in any direction

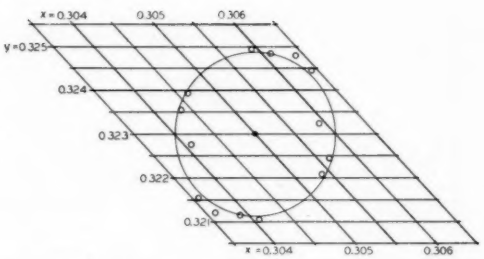

FIG. 5. Oblique I.C.I. coordinate system for restricted chromaticity range, within which equal distances correspond to equally noticeable chromaticity differences.

corresponds to the standard deviation of color matching, if each increment of x is represented by the distance $(g_{11})^{\frac{1}{2}}\Delta x$, and if each increment of y is represented by the distance $(g_{22})^{\frac{1}{2}}\Delta y$. The experimental points from which one of the noticeability ellipses was determined are plotted in the corresponding oblique coordinate system in Fig. 5. In this region, $g_{11}=102\times10^4$, $g_{12}=-50\times10^4$, $g_{22}=53\times10^4$. Therefore, the angle between the oblique coordinate axes is given by

$$\cos \omega = -50/(102\times53)^{\frac{1}{2}} = -0.679, \quad \omega = 132.8°.$$

The lengths of the scale increments, $\Delta x = \Delta y = 0.001$ are $0.001(102\times10^4)^{\frac{1}{2}} = 1.01$ and $0.001(53\times10^4)^{\frac{1}{2}} = 0.73$. A circle of unit radius is drawn through the experimental points in Fig. 5. The departures from this circle are only slightly more serious than the departures from the ellipse previously drawn through the corresponding points plotted in the standard I.C.I. diagram.

Within the region for which this coordinate system is appropriate, that is, within which g_{11}, g_{12}, and g_{22} do not change by more than 25 percent, the ordinary metrical properties of plane geometry are applicable to the chromaticities represented. Thus, the closest match to a given chromaticity, chosen from among a series represented by a smooth continuous locus in this region, is represented by the foot of the perpendicular on the locus drawn through the fixed point. Similarly, six chromaticities as noticeably different from a central color as from each other are indicated by the vertices of a regular hexagon inscribed in a circle whose center is the fixed color and whose radius represents the noticeability of the equal chromaticity differences.

The appropriate oblique coordinate system should be constructed for each region of interest.

Kinds and degrees of chromaticity differences can be satisfactorily represented in this manner only within regions for which the coefficients, g_{11}, g_{12}, and g_{22} do not change by more than about 25 percent. Specifications of greater chromaticity differences require assumptions concerning the perceptual significance of the integration of small chromaticity differences, and consideration of the fact that straight lines in the I.C.I. diagram are not, in general, the geodesic paths containing the least number of noticeable steps between two terminal chromaticities.[2] The specification of large chromaticity differences is fraught with great theoretical as well as practical difficulties. It is suggested that such specifications be avoided if possible, or attempted only with great caution.

If the I.C.I. chromaticity diagram is subdivided into neighboring rectangles (for each of which g_{11}, g_{12}, and g_{22} are practically constant) and each of these is represented by the corresponding parallelogram in which the noticeability ellipse becomes a unit circle, and if these parallelograms are assembled in the order corresponding to their counterparts in the I.C.I. diagram (with appropriate trimming and fitting, corresponding to the variations of g_{11}, g_{12}, g_{22}), a curved surface of complicated shape will be constructed.* On this "true color surface" equal distances represent equal noticeabilities. The geodesic paths on this surface do not correspond to straight lines in the I.C.I. diagram, the sums of the angles of geodesic triangles do not equal 180°, and the curvature of this surface is not constant but attains quite significantly different values, both positive and negative. The effects of the curvatures of this surface are not troublesome when comparisons are made between chromaticities confined to any region within which g_{11}, g_{12}, g_{22} do not vary by more than 25 percent, but the curvatures greatly complicate and perhaps invalidate the specification of much larger chromaticity differences.

The effects of changes of luminance of the test field, of various contrasts with the surrounding field, of various chromaticities in the surrounding field, and of simultaneous variations of luminance and chromaticity between the halves of the test field are being investigated, and attempts will be made to extend Eq. (5) to include such effects.

* Dr. Silberstein suggested this method of construction.

Helmholtz,[3] Schrödinger,[4] Sinden,[5] and Silberstein[2] have speculated concerning the kinds of modification of such equations which may be appropriate when luminance and chromaticity are simultaneously variable. The additional effects of background contrast and chromaticity have been discussed by Bouma[6] and Spencer.[7] The applicability of the ideas of these authors cannot be decided on the basis of the present data and it appears that suitable modifications of Eq. (5) must await the accumulation and study of extensive additional observations.

APPENDIX CONCERNING THE METRICS OF PLANE PROJECTIVE TRANSFORMATIONS

The possibility that equally noticeable chromaticity differences might be represented by equal distances in some plane projective transformation of the I.C.I. diagram has been suggested by several authors.[8–13] In such a case, the ordinary metric properties of plane geometry would be immediately applicable to chromaticities represented in the transformed diagram. The curved surface resulting from the construction just described is not developable on a plane, consequently the possibility suggested cannot be realized. The present author has discussed certain other conditions which can be tested more directly and which must be fulfilled, if a uniform representation of noticeability of chromaticity differences is possible in a plane projective transformation of the I.C.I. diagram. The methods of differential geometry confirm and extend the results previously published.[14] In the previous article, the following equations were shown to be adequate for the representation of any plane projective transformation of the I.C.I. (x, y) diagram.

$$u = c_3 + (e_1x + e_2y)/(c_7x + c_8y + 1), \tag{8a}$$

$$v = c_6 + (e_4x + e_5y)/(c_7x + c_8y + 1). \tag{8b}$$

[6] P. J. Bouma, "Grundlagen einer allgemeinen Theorie der Farbenmetrik," K. Akad. v. Wetenschappen Amst. Afdeel. Nat. **38**, 35–45, 148–166, 258–281 (1935).

[7] D. E. Spencer, "Adaptation in color space," J. Opt. Soc. Am. **32**, 632A (1942).

[8] T. Smith, "The colour triangle and colour discrimination," *Discussion on Vision* (Physical Society, London, 1932), pp. 212–226.

[9] D. B. Judd, "A Maxwell triangle yielding uniform chromaticity scales," J. Opt. Soc. Am. **25**, 24–35 (1935).

[10] D. B. Judd, "Estimation of chromaticity differences and nearest color temperature on the standard 1931 I.C.I. colorimetric coordinate system," J. Opt. Soc. Am. **26**, 421–426 (1936).

[11] F. C. Breckenridge and W. R. Schaub, "Rectangular uniform-chromaticity-scale coordinates," J. Opt. Soc. Am. **29**, 370–380 (1939).

[12] F. Scofield, D. B. Judd, and R. S. Hunter, "A proposed method of designating color," Bull. A.S.T.M. 19–24 (May, 1941).

[13] W. D. Wright, "The sensitivity of the eye to small colour differences," Proc. Phys. Soc. London **53**, 93–112 (1941).

[14] D. L. MacAdam, "Projective transformations of color-mixture diagrams," J. Opt. Soc. Am. **32**, 2–6 (1942).

The coordinates u and v defined by these equations may be represented in either oblique or rectangular coordinate systems. If a rectangular coordinate system with equally divided scales of u and v is employed, the distance element ds satisfies the relation

$$ds^2=du^2+dv^2. \tag{9}$$

If equal distances in the transformed chromaticity diagram correspond to equally noticeable color differences, then this distance element is proportional (or equal) to the measure of noticeability defined by Eq. (5). Under these conditions

$$g_{11}=(A_1+A_4y^2+2A_5y)/(c_7x+c_8y+1)^4, \tag{10a}$$
$$g_{12}=(A_2-A_4xy-A_5x-A_6y)/(c_7x+c_8y+1)^4, \tag{10b}$$
$$g_{22}=(A_3+A_4x^2+2A_6x)/(c_7x+c_8y+1)^4, \tag{10c}$$

where

$$A_1=e_1^2+e_4^2,$$
$$A_2=e_1e_2+e_4e_5,$$
$$A_3=e_2^2+e_5^2,$$
$$A_4=A_1c_8^2-2A_2c_7c_8+A_3c_7^2,$$
$$A_5=A_1c_8-A_2c_7,$$
$$A_6=A_3c_7-A_2c_8.$$

The expressions for A_1, A_2, and A_3, and the constants c_7 and c_8 were shown previously to be invariant for all transformations yielding the same shape spectrum locus and identical metrics within the color domain.[14] Therefore, the expressions for A_4, A_5, and A_6 are also invariant under the same circumstances. The occurrence of invariant coefficients in the expressions for g_{11}, g_{12}, g_{22} is a consequence of the fact that the noticeability data should determine and should be fully represented by the metrical properties (not dependent upon location or orientation relative to the coordinate axes) of the plane projective transformation, if equal distances in such a transformed diagram can successfully represent equally noticeable chromaticity differences. The coefficients, g_{11}, g_{12}, and g_{22} defined by Eqs. (10) are constant along fourth-degree curves in the I.C.I. diagram. The values of the coefficients derived from observations and used in the construction of Figs. 1, 2, and 3 cannot be represented adequately by systems of contours consisting of fourth-degree curves related to each other as specified by Eqs. (10). Consequently, the noticeability ellipses from which Figs. 1, 2, and 3 were derived cannot be represented adequately by circles of equal radius in any plane projective transformation of the I.C.I. chromaticity diagram. Further, if Eqs. (10) were adequate representations of coefficients in Eq. (5), then the noticeability ds corresponding to any segment (defined by dx) of a straight line $(y=mx+B_1)$ in the I.C.I. chromaticity diagram would be given by

$$ds=B_2dx/(c_7x+c_8y+1)^2, \tag{11}$$

where

$$B_2^2=A_1+2A_2m+A_3m^2+A_4B_1^2+2A_5B_1-2A_6B_1m.$$

If D represents the distance $[(x-x_0)^2+(y-y_0)^2]^{\frac{1}{2}}$ along the straight line $(y=mx+B_1)$ from its intersection x_0, y_0 with the line $(c_7x+c_8y+1=0)$, then Eq. (11) becomes

$$ds=B_3dD/D^2, \tag{12}$$

where

$$B_3^2=(1+m^2)B_2^2/(c_7+c_8m)^4.$$

This equation asserts that for equal noticeability of the corresponding chromaticity differences, the lengths (dD) of the segments of the line $(y=mx+B_1)$ are proportional to the square of the distance (D) from the intersection of that line with the line $(c_7x+c_8y+1=0)$ which is projected to infinity by the plane projective transformation.[14] Many series of equally noticeable chromaticity differences have been observed which are not represented adequately by equations of the form of Eq. (12). This is perhaps the most direct and most easily confirmed evidence that uniform representation of noticeability of chromaticity differences is not possible in any plane projective transformation of the standard I.C.I. diagram.

Applications of Near Infra-Red Spectrophotometry

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(Received August 19, 1942)

The commercial General Electric spectrophotometer has been modified so as to afford automatic recording over the range 375–1200 mμ. This extended range has been found useful in the analysis of colorless materials, the identification of dyes, and the formulation of infra-red paints.

INTRODUCTION

THE General Electric automatically recording visual range spectrophotometer was originally designed to cover the range 400–700 mμ. There are some instances where even a slightly extended range is highly desirable. Thus with some dyes such as Direct Fast Yellow B in water solution the absorption maximum falls below 400 mμ. Similarly with Indanthrene Blue RS in sulfuric acid the absorption maximum is above 700 mμ. For certain purposes, for instance in determining the concentration of dye present, it is desirable to know the transmission at the absorption maximum. Hence there is a natural desire to extend the range somewhat and include these regions just outside of 400–700 mμ.

APPLICATIONS

The usefulness of the near infra-red region has been generally appreciated[1–5] and several abridged spectrophotometers of the manually

[1] P. W. Cunliffe, J. Soc. Dyers and Colourists **49**, 73 (1933).
[2] P. W. Danckwortt, Zeits. f. angew. Phot. **1**, 48 (1939).
[3] M. Farnsworth, Tech. Studies **7**, 88 (1938).
[4] J. Grant, Textile Colorist **64**, 213 (1942).
[5] I. G. Priest, J. Opt. Soc. Am. **4**, 388 (1920).

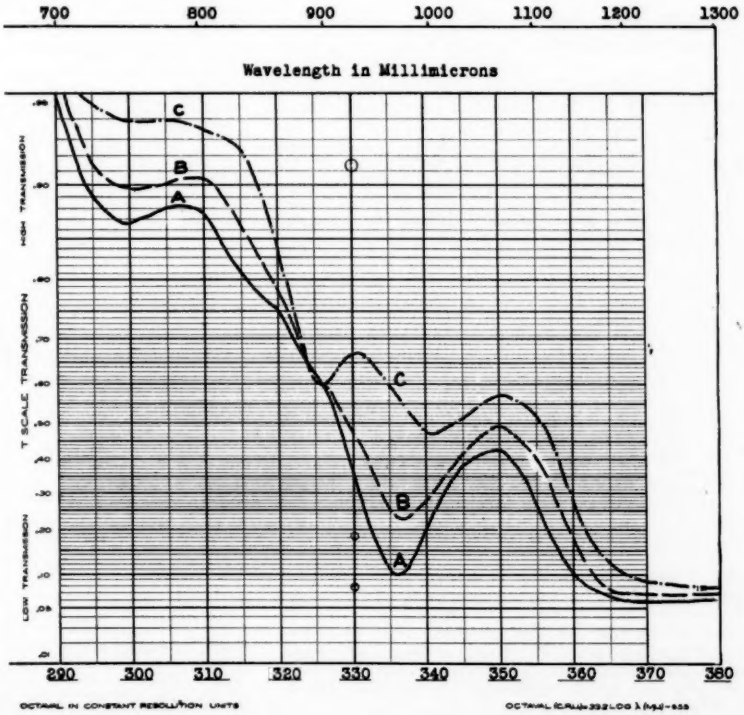

FIG. 1. Analysis of water in ethanol mixture: a. water, b. mixture of 50 percent water and 50 percent ethanol, c. ethanol.

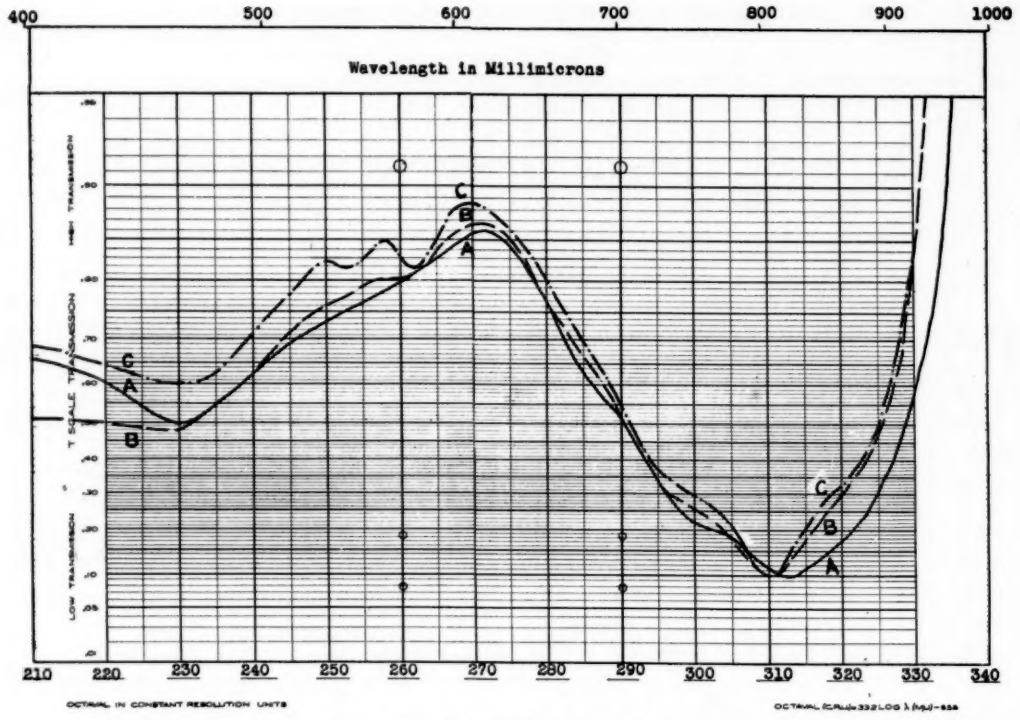

FIG. 2. Differentiation of dyes: a. Indanthrene Blue RS, b. Indanthrene Blue GCD, c. Indanthrene Blue GCS.

recorded type have covered an extended range from approximately 200–1000 mμ.

Figure 1 illustrates the applicability of the near infra-red range to the analysis of colorless materials. At 335 c.r.u.[6] (960 mμ) ethyl alcohol has an extinction coefficient of 0.22 and water has an extinction coefficient of 0.96 square centimeter per gram. This means that with the assistance of a five times magnifying ordinate cam, it is possible to determine the amount of water in alcohol with a sensitivity of about 0.2 percent by a spectrophotometric measurement requiring less than five minutes.

Figure 2 illustrates an application of the near infra-red range in the analysis of dyes. The three dyes shown are Indanthrene Blue RS (CI 1106), Indanthrene Blue GCD (CI 1113), and Indanthrene Blue GCS (CI 1114). These differ only in their chlorine content which increases in the ratio 0, 2, 3 atoms per molecule, respectively. The addition of the region around 310 c.r.u. to the visual range facilitates the differentiation of these three products.

Figure 3 illustrates the use of the near infra-red range in reflectance measurements. The two pigments shown are Phthalocyanine Blue and Chrome Oxide. With a complete file of pigment curves it is possible to formulate paints having any desired infra-red reflecting properties.

PRECAUTIONS

With a machine sensitive over an extended range some sources of error are found which are not a problem when only the restricted 400–700 mμ range is used. For instance, Fig. 4 shows two measurements of Naphthalin Green V (CI 735), one taken with the RCA 929 photo-cell and one taken with the RCA 925 photo-cell.

[6] Note: A c.r.u. is a unit in the octaval system of designating radiant energy. Octaval corresponds to logarithm of wave-length and is related to wave-length in millimicrons (λ) in the following manner. Octaval (c.r.u.) $=332.19 \log_{10}\lambda(m\mu)-655.07$. Being a logarithmic unit, c.r.u. is dimensionless. One c.r.u. corresponds to 1/100th of a spectral octave. See W. A. Shurcliff, J. Opt. Soc. Am. **32**, 229 (1942).

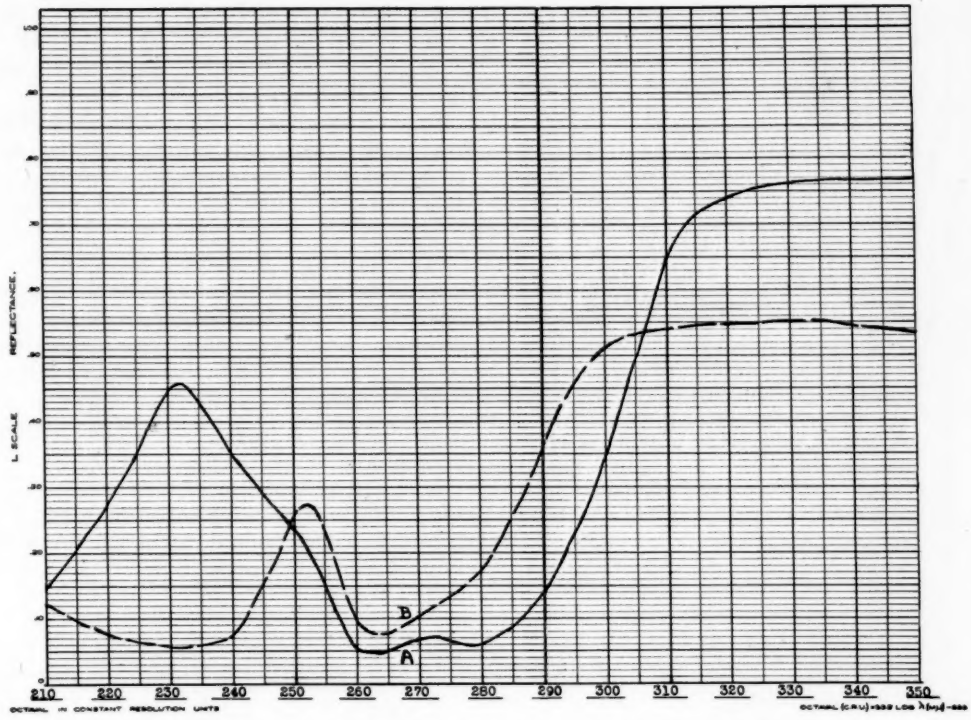

FIG. 3. Reflectance measurements: a. Phthalocyanine Blue, b. Chrome Oxide Green.

This dye is fluorescent, that is, light of 277 c.r.u. is absorbed and re-emitted as infra-red radiation. The 929 cell, having no response to the re-emitted fluorescent radiation, plots the true 277 c.r.u. absorption. On the other hand the 925 cell, being sensitive to the infra-red, plots a false apparent reflection which is the sum of (1) the true reflected light of 277 c.r.u. and (2) the re-emitted fluorescent radiation. The fluorescence of this dye might be overlooked because it is not visible.

EQUIPMENT UTILIZED

Early in our experience it was found desirable to alter the amplifier system of the original commercial spectrophotometer and develop an amplifier which worked in conjunction with a Type RCA 929 photo-cell.[7] This photo-cell is interchangeable with Type RCA 925. These photo-cells are sensitive over the approximate range 300 mμ to 800 mμ, and 450 mμ to 1200 mμ.

Accordingly only mechanical difficulties prevented the making of measurements from 375 mμ where the energy of the tungsten light source failed to 1200 mμ where the sensitivity of photocell RCA 925 failed. The mechanical difficulty was that the selector slit on the spectrophotometer was pushed by a cam only over the range 400–700 mμ.

As a preliminary test, two glass prisms were inserted in the light path, one between the first dispersing prism and the selector slit, the other symmetrically between the second dispersing prism and the selector slit. When these were oriented so as to reduce the deviation caused by the dispersing prisms, the near ultraviolet part of the spectrum was displaced into the range covered by the slit. When oriented oppositely, so as to increase the deviation, the near infra-red part of the spectrum was passed by the slit. Thus a workable extension was obtained.

[7] R. H. Park, American Dyestuff Reporter **29**, 272 (1940).

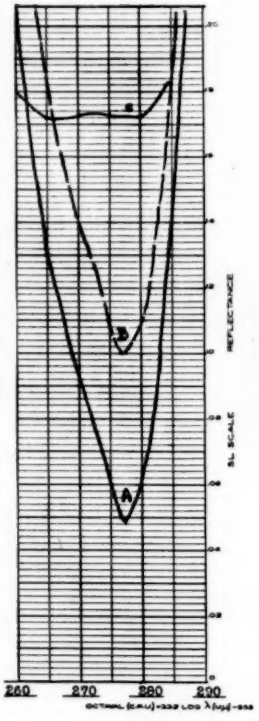

FIG. 4. Infra-red fluorescence of Naphthalin Green V: a. visual range photo-tube RCA 929, b. infra-red range photo-tube RCA 925, c. non-fluorescent sample which plots identically with either photo-cell.

As a second modification, also in a preliminary way, alternate mid-slit push rods were constructed. When the shorter than normal push rod was used to transfer motion from the wave-length cam to the slit carriage, the near ultraviolet was passed by the slit, and when the longer than usual push rod was used, the near infra-red was passed by the slit. In using the different push rods to move the mirror carriage, the slit width cam was disconnected.

Both of these preliminary schemes had the disadvantage that the abscissa scales were purely arbitrary. The ultraviolet range was very much stretched out and the infra-red range very much compressed. This was a necessary consequence of the fact that a wave-length cam designed for the spectral dispersion in the range 400–700 mμ was being used for all ranges.

Finally therefore, a new wave-length cam, linear in log wave-length, was constructed (see Shurcliff, reference 6), which cam was used in obtaining the data of the figures presented herewith.

To facilitate changing photo-cells for the two ranges the back of the integrating sphere was made removable. Thus it is possible to change from one range to another in twenty seconds.

CALIBRATIONS

In order to calibrate the abscissa cam the absorption peaks of a didymium filter at 310.4 c.r.u. (806 mμ) and 323.1 c.r.u. (880 mμ) were used. The location of these peaks was determined by measurements on a medium Hilger spectrograph. In addition the emitted mercury line at 343.52 c.r.u. (1014 mμ) was used for calibration. This was done by using a mercury arc as a light source in the spectrophotometer.

A Method for Determining Depolarization Factors in Raman Spectra

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(Received October 8, 1942)

A method is described for the measurement of depolarization factors in Raman spectra which utilizes the spectral intensity traces obtained directly on a recording monochromator. A dry ice-refrigerated multiplier photo-tube is used as a detector with additional d.c. amplification. The initial photo-current, amplified some 10^8-fold, is continuously traced on a galvanometer deflection recorder of sensitivity 10^{-9} amp./mm. Analysis of the partially polarized scattered Raman light is made by means of a Polaroid oriented to obtain one record each for the parallel and perpendicular intensities. The instrument responds to the parallel and perpendicular intensities in the ratio of 0.82 to 1.00. Thus, the apparent depolarizations determined by this method were divided by 0.82 to correct for the inequivalence of transmission by the instrument for the two types of polarization. Values thus obtained for the principal Raman lines of benzene, chloroform, carbon tetrachloride, and symmetrical tetrachloroethane are tabulated together with results published by other authors. Values obtained for the depolarization factors ρ agree satisfactorily with the values for the same molecules using the generally accepted method of Cabannes and Rousset.

IDENTIFICATION of the modes of vibration of the atoms in a molecule is largely facilitated if the depolarizations of the lines in the Raman spectrum of that molecule are known. Cabannes[1] and his co-workers have developed satisfactory technique for making depolarization measurements. Cabannes and Rousset[2] have given a complete description of the method they have used. The above-mentioned method of measurement should give the proper value for the depolarization factor of the Raman lines. However, this experimental technique requires the skillful use of a rather complicated optical arrangement to produce satisfactory results. It is well known that the light intensity available, which is small at best in Raman spectra, is much reduced in the parallel light arrangement used by Cabannes and his co-workers.

Placzek and Van Wijk[3] have described a method of making depolarization measurements which is essentially the same as that of Cabannes as far as the analyzing of the polarized light is concerned. The method of excitation of the spectra is, however, Wood's method rather than the parallel light arrangement. In Wood's method of excitation the incident light is neither parallel nor incident at right angles to the observed scattered light. The advantage of using Wood's method of excitation is obvious, since the intensity of the scattered light is enormously greater than when excited by the parallel light method. Placzek and Van Wijk have pointed out that measurements of polarizations made using Wood's method of excitation are in error. The absolute values of the depolarization factors obtained by Placzek and Van Wijk differ widely from the theoretically correct values for highly polarized lines. However, the last-mentioned authors have shown that a correlation can be drawn between the results obtainable by their method and the results obtained by the parallel light method of Cabannes.

All methods which have been used up to the present time for determining depolarization factors in Raman spectra, have made use of photographic photometry for the measurement of the relative intensity of the polarized components of the Raman line in question. It seemed desirable, upon development of a direct photoelectric technique of intensity measurement in Raman spectra,[4] to make use of this tool to measure depolarizations.

Employment of a direct photoelectric method of intensity measurement of the polarized com-

[1] J. Cabannes, Comptes rendus **187**, 654 (1928).
[2] J. Cabannes and A. Rousset, Ann. de physique **19**, 229 (1933).
[3] G. Placzek and W. R. Van Wijk, Zeits. f. Physik **67**, 582 (1931).
[4] D. H. Rank, R. J. Pfister, and P. D. Coleman, J. Opt. Soc. Am. **32**, 390 (1942).

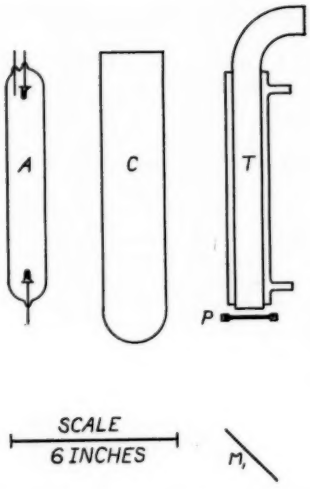

FIG. 1. Schematic diagram of light source and optical appurtenances for measurement of depolarization factors. *A*, mercury arc; *C*, cylindrical lens; *T*, scattering tube; *P*, Polaroid disk; M_1, plane mirror.

ponents of the Raman lines would be almost impossible if it was necessary to resort to the parallel light method of excitation of the spectra as used by Cabannes and his co-workers. The work of Placzek and Van Wijk shows the practical feasibility of using a method of excitation other than a theoretically perfect one for determining depolarization constants.

EXPERIMENTAL

The experimental arrangement used to measure depolarizations is essentially that described in an earlier paper.[4] Since the geometry of light source and appurtenances will to some extent regulate the values obtained for the depolarization factors, the experimental arrangement of light source, etc., is shown in Fig. 1 drawn to scale. The arc *A* was a 400-watt Westinghouse high intensity a.c. Hg arc lamp. The lamp was supplied with a.c. by means of a suitable transformer operated on a 1000-watt Raytheon voltage regulator which in turn was supplied from the power mains. The light intensity of the lamp could be maintained constant to 1 or 2 percent for several hours at a time. Figure 1 shows the arc in a vertical position. *C* is a Pyrex tube which in these experiments contained water as the refracting medium. Light from the arc *A* falls on *C* which acts as a cylindrical lens, focusing a line image of the light source in the scattering tube *T*. The scattering tube was surrounded with a water jacket to prevent excessive heating of the sample under investigation. The volume of liquid necessary for filling the scattering tube was 80 cm^3.

It can be seen by reference to Fig. 1 that the convergent light brought to a focus by the cylindrical lens builds a "trace" in the scattering tube. This "trace" when viewed end on has the appearance of a relatively narrow line. A front surface aluminized mirror M_1 is used to turn the direction of the scattered light through a right angle. Light emerging from the scattering tube and reflected by the plane mirror is collected by a lens of suitable aperture. The lens then focuses an end-on image of the scattered "trace" on the slit of the monochromator. A Polaroid *P* was placed in the position indicated in Fig. 1. The Polaroid* was mounted so that it could be rotated to extinguish either parallel or perpendicular vibrations at will. The large grating monochromator, photo-multiplier, amplifier, and galvanometer deflection recorder were the same as described in an earlier paper.[4]

In order to increase the usable sensitivity of the photoelectric cell a suitable housing has been constructed so that the cell can be refrigerated with solid CO_2. Furthermore, a condenser of 0.01-μf capacity was shunted across the output of the photo-multiplier tube. Introduction of the condenser in the circuit smoothes out the fluctuations of the output by increasing the time constant of the circuit. Making use of cooling and increased time constant it has been possible to reduce the random fluctuations to less than one-tenth the value given in our previous paper. The present limit of detection is a photo-current

* The reason for placing the Polaroid in the position indicated in Fig. 1 is obvious. The most convenient place would be to insert the Polaroid in the convergent beam in front of the slit of the monochromator. At the surface of the reflecting mirror elliptical polarization takes place. Thus, if the Polaroid were placed in front of the slit it would not be able to extinguish this "manufactured" elliptically polarized light and in this manner introduce a serious error in the determination of the value of ρ. Substitution of a right-angled totally reflecting prism for the plane aluminized mirror would not remove this difficulty. As an example, for CCl_4 $\Delta\nu - 459$ cm^{-1}, $\rho = 0.07$ with the Polaroid in position in front of the window of the scattering tube. With the Polaroid in position in front of the slit the value of $\rho = 0.33$ was obtained for this line.

of approximately 5×10^{-17} ampere. The speed of rotation of the grating has been reduced so that 5 angstroms per minute pass by the exit slit of the monochromator. This reduction of driving speed has, of course, been necessitated by the increased time constant of the electrical circuit. It is significant to note that an over-all amplification of 10^8 is used in conjunction with a recording galvanometer of 10^{-9} ampere per mm sensitivity at 4 meters.

Theoretically, in order to determine depolarization factors in Raman spectra two conditions with regard to the incident light should be fulfilled.

1. The light incident on the scattering sample should be parallel.
2. The incident light should be unpolarized.

Angus, Ingold, and Leckie[5] have used convergent light in determining the depolarization factors of the Raman lines of the benezenes. Making use of a correction formula for the depolarization factor (ρ) due to Ananthakrishnan,[6] Angus, Ingold, and Leckie were able to correct their measured values of ρ so as to make these values conform to the theoretically expected values and also to conform to the values as measured using the experimental method of Cabannes and Rousset.

The apparatus which has been described in this paper can be seen to make use of convergent light to illuminate the scattering sample. An experiment was performed introducing a Soller slit system between the arc and cylindrical lens to reduce the vertical convergence of the incident beam of light. The slit system made the light parallel vertically to 5°. No difference was detectable in the values obtained for ρ with and without the use of the Soller slit system.

It can be seen on inspection that the cylindrical lens used in the apparatus partially polarizes the light incident on the sample. It was to be expected and was noted experimentally that the light reflected from the glass surface of the cylindrical lens was strongly polarized. The light transmitted by the cylindrical lens was polarized in such a fashion that the ratio of the horizontal to the vertical vibrations as measured by means of a Polaroid and photronic cell gave a value of 1.05.

Convergence and polarization of the incident light in the apparatus described above apparently act in such a fashion so as nearly to neutralize each other with respect to their behavior in modifying the depolarization factor. The values obtained directly for the ratio of the intensity of the parallel to the intensity of the perpendicularly polarized beam due to a Raman line agree well with the theoretically expected values and also with the values obtained by other investigators using generally accepted methods of measurement. The above result is in contradistinction to the results of Placzek and Van Wijk who have used the Wood's light furnace method of excitation. It must also be stated that with the apparatus used in the present investigation a metal reflector was placed in such a position on the jacket of the scattering tube so as to reflect the incident light back through the scattering tube. The effect of the metal reflector was nearly to double the intensity of the scattered light. No appreciable difference was found in the value of ρ determined with or without the use of the reflector. Since the intensity was ample in the cases which were investigated in the present paper no reflector was used in determining any of the values of ρ given in this paper.

It is well known that a prism spectrograph will transmit one kind of plane polarized light more freely than the other kind. In making depolarization measurements, when a Wollaston prism is used it is customary to insert a half-wave plate in the one polarized beam to convert both beams of polarized light produced by the Wollaston prism into identical polarizations. Thus the differential transmission of the spectrograph for different kinds of plane polarized light is eliminated. The apparatus used in the present investigation does not suffer seriously from the above-mentioned selective transmission defect so troublesome in prism spectrographs. The optical parts of the monochromator are all front surface mirrors and the dispersing device is an aluminum diffraction grating. The following experiment was performed to test the equivalent transmission of parallel and perpendicularly polarized light. A flashlight bulb was placed in

[5] W. R. Angus, C. K. Ingold, and A. H. Leckie, J. Chem. Soc. 926 (1936).
[6] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **A2**, 133 (1935).

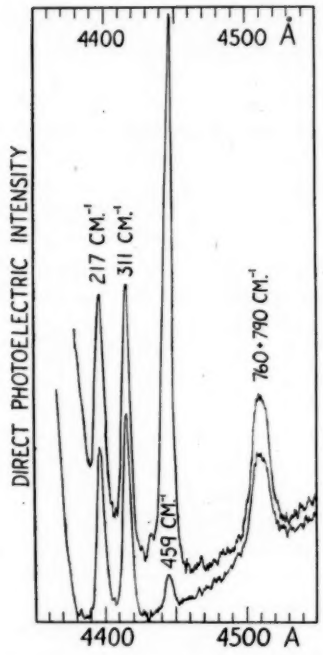

FIG. 2. The perpendicular and parallel spectral intensity traces of the Raman lines of carbon tetrachloride. Two successive records were taken with an f:4.5 recording monochromator, the first with the Polaroid set to transmit the perpendicular intensity and the second with the Polaroid set to transmit the parallel intensity.

the position normally occupied by the window of the scattering tube. The Polaroid was oriented to transmit parallel polarized light and the galvanometer deflection read. Similarly the response obtained with the perpendicularly polarized beam was measured. The result of this experiment shows that the ratio of the intensity of the parallel to the perpendicular beam is 0.82. This same transmission ratio was found by measuring the intensities of the polarized components of the Hg exciting light scattered from white paper.

The method of procedure in measuring the depolarization of the Raman lines was to make a recording of the Raman spectrum with the Polaroid first placed to transmit the parallel intensity and then a second recording was made with the Polaroid in the position to transmit the perpendicular intensity. Two of such spectral intensity traces for the Raman lines of carbon tetrachloride are shown in Fig. 2. A comparison of the two curves for the 459-cm^{-1} shift line shows this frequency to be almost completely polarized whereas the other lines are only partially polarized or not polarized at all (depolarized). The heights of the line peaks above the adjacent background were measured from the records, and the ratio of the parallel intensity to the perpendicular intensity was taken to yield the value of the apparent depolarization factor ρ'. It may be seen that the apparent depolarization must be corrected by dividing by 0.82 to account for the non-equivalence of transmission of the instrument for the two kinds of plane polarized light. These corrected values of ρ are given in column headed Rank, Pfister, and Grimm in Table I.

The continuous background accompanying the line spectrum was found to be strongly polarized especially in the case of scattering from carbon

TABLE I. A comparison of values of depolarization factors determined by various authors.

Frequency shift, cm^{-1}	Placzek and Van Wijk[a]	Cabannes and Rousset[b]	Angus, Ingold and Leckie[c]	Trumpy[d]	Rank Pfister and Grimm
		Benzene			
605	0.99	D	0.81		0.78
849	.90	D	.77		.78
992	.35	0.07	.09		.09
1178	.78	D	.70		.63
1584		D	.81		
1606	.99	D	.81		.81
3047		D	D		
3062	.49	0.40	.4		.34
		Carbon tetrachloride			
217	0.90	0.83			0.93
311	.91	.79			.88
459	.45	.05			.07
760		6/7			
790	.95	6/7			.80
		Chloroform			
261		0.70			0.88
366		.22			.24
667		.06			.05
758		.68			.89
1209		6/7			D
3020		.32			.33
		Symmetrical tetrachloroethane			
171				0.62	D
241				.60	0.84
289				.7	.84
351–365				.14	.25
546				D	.70
648				.05	.11
800				.51	.61
2986				.30	.40

[a] See reference 3. [c] See reference 5.
[b] See reference 2. [d] See reference 7.

tetrachloride. This continuum is largely produced by unmodified scattering by the liquid and it showed a depolarization factor of 0.7. It is interesting to compare the background of the two polarized components of carbon tetrachloride shown in Fig. 2. As the monochromator records the spectral intensities in the neighborhood of the exciting line the perpendicular intensity will be seen to rise rapidly while the parallel intensity still remains low. This is the result of a partial polarization of the exciting line and a preferred transmission of the instrument for the perpendicular intensity over the parallel intensity.

DISCUSSION OF RESULTS

The values determined for the depolarization factors of the Raman lines of benzene, carbon tetrachloride, chloroform, and symmetrical tetrachloroethane are given in Table I. The headings of the columns in Table I denote the source from which the measurements of ρ were taken. The last column gives the measurements made by the present authors. The resolving power used in the present investigation did not permit the separation of doublets closer than about 40 cm^{-1}. All lines whose depolarizations were measured were excited by λ4358 of mercury or by λ4047. The agreement of the results obtained in the present investigation with the results obtained by Cabannes and Rousset is fairly satisfactory. The agreement with Trumpy[7] for symmetrical tetrachloroethane is not quite as good, but certainly tolerable. In conclusion it appears that the method of measuring depolarizations described in this paper yields results nearly identical with those obtained using the strictly correct method of Cabannes and Rousset.

We wish to express our appreciation to the Pennsylvania Grade Crude Oil Association for the financial assistance furnished to one of us.

[7] B. Trumpy, Zeits. f. Physik **93**, 624 (1934).

JANUARY, 1943 J. O. S. A. VOLUME 33

On Size-Frequency Distribution in Photographic Emulsions*

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THE silver halide crystals or "grains" composing a photographic emulsion are microscopic flat targets, triangular, pentagonal, hexagonal, or rounded off to almost circular disks. The shape of these light targets, however, is of lesser importance for the photographic properties of the emulsion than their *size*, that is to say, their effective area. This "size," say x, is in general not nearly equal for all grains but varies within more or less wide limits. The photographic properties of an emulsion depend not only on the average or mean size $\bar{x}$ but also on the distribution of sizes among the grains. The student of photography is, therefore, interested in the peculiarities of such a distribution which vary from emulsion to emulsion according to the precipitation time and other details of the process of emulsion making.

A fair sample of the emulsion, consisting in all of n grains (usually about a thousand), is divided into a number of classes, usually ranging in size from nil (or 0.02) to $0.1\mu^2$, from 0.1 to 0.2, from 0.2 to $0.3\mu^2$, and so on, and the grains falling into each of these classes are actually counted. Let x stand, henceforth, for the mean class size, and let f be the frequency or the number of grains falling into any one of these classes. Then, what is called the size-frequency distribution of the emulsion is the set of numbers

$$f=f(x),$$

which satisfy, of course, the condition $\Sigma f(x)=n$, the sum being extended over all classes.

The corresponding graph is the familiar histogram (a sequence of contiguous rectangles) or a discrete set of points with equally spaced abscissae x_1, x_2, etc., the mean class sizes, and the counted numbers $f(x_1)$, $f(x_2)$, etc., as ordinates.

Let Δ be the finite width of each class and $g(x)$

* Communication No. 873.

a generally continuous function of x, such that $g(x)dx$ is the number of grains of size x to $x+dx$. Then any of the frequencies found by actual counting is

$$f(x_i)=\int_{x_i-\frac{1}{2}\Delta}^{x_i+\frac{1}{2}\Delta} g(u)du.$$

Owing to the finite class width, the points having the ordinates $f(x_i)/\Delta$ will not lie on the curve $g=g(x)$, but a little above or below it. In fact, up to higher terms in Δ, we have

$$\frac{1}{\Delta}f(x_i)-g(x_i)=\frac{\Delta^2}{6}g''(x_i),$$

or, with Δ taken as the unit of x,

$$f(x_i)-g(x_i)=\tfrac{1}{6}g''(x_i).$$

Under the actual conditions, however, this deviation is not of much importance, so that the continuous distribution curve $g=g(x)$ may be confounded with a smooth curve drawn through, or close to, the observed frequency points $f(x_i)$.

Of some importance is the effect of the finiteness of the sample or of the total number n of grains counted upon the observed frequencies f as representatives of the actual composition of a huge mass of the emulsion, containing (say) many millions of grains.

The probable error of any of the frequencies f (observed on a sample of n grains in all) as representative of the composition of a large amount of the emulsion is

$$\text{p.e.}(f)=\pm 0.477[2f(n-f)/n]^{\frac{1}{2}}. \qquad (1)$$

This formula, whose simple derivation from the principles of the calculus of probabilities need not detain us here, will be utilized in the sequel. For a fixed n, the probable error attains its maximum for $f=n/2$, *viz.*, $\text{p.e.}(n/2)=\pm 0.477(n/2)^{\frac{1}{2}}$. The fraction of grains of this class contained in a huge mass of the emulsion is thus $\frac{1}{2}$ with the probable error

$$\pm 0.477/(2n)^{\frac{1}{2}}.$$

If, for instance, $n=1000$, this probable error amounts to 0.011 or a little more than 2 percent of that fraction.

Numerous size-frequency curves have been found experimentally in these Laboratories by actual planimetrization and counts of the enlarged grains, for a great variety of photographic emulsions, and many attempts have been made to represent the experimental findings by a distribution function $f(x)$ of a more or less simple form.

As in many other branches of statistics, the first to suggest itself was the so-called "normal" or Gaussian distribution function

$$f(x)=f_m \exp\left[-c^2(x-x_m)^2\right], \qquad (G)$$

where c^2 is some positive constant and x_m the most frequent grain size. The corresponding curve, with x as abscissa, is of course *symmetrical* with respect to its maximum ordinate $f_m=f(x_m)$. Extended trials, however, have shown that this function is, generally,[1] far from representing satisfactorily the size-frequency curves actually observed on photographic emulsions. Most of these curves, in fact, are emphatically asymmetrical, always with x (size, area) as abscissa.

The next distribution function, suggested and extensively applied by Mr. R. P. Loveland[2] of these Laboratories, was Kapteyn's function which is simply the Gaussian function of $\log x$ instead of x itself, *viz.*,

$$f(x)=f_m \exp\left[-c^2(\log x-\log x_m)^2\right]$$
$$=f_m \exp\left[-c^2 \log^2 (x/x_m)\right]. \qquad (K)$$

The corresponding curve, being symmetrical with $\log x$, is of course asymmetrical with x itself as abscissa. For the reasoning which has led the famous Dutch astronomer to this form which offers many points of general interest, the reader must be referred to his and Dr. Van Uven's original publication.[3] Without embarking here upon a discussion of that reasoning, we should like to point out only that Kapteyn's function has the remarkable and perhaps useful property of retaining its form when x is replaced by any power of x, as, e.g., by $\sqrt{x}$ and thus by a diameter of the grains. For such a change introduces only a constant numerical factor which may be thrown upon the coefficient c^2. (This obvious property has also been mentioned by Loveland and Tri-

[1] With the exception, perhaps, of some Lippmann emulsions quite recently investigated with the aid of the electron microscope; but even these show an approximately "normal" distribution of diameters, and thus ultimately of $\sqrt{x}$ rather than x.

[2] R. P. Loveland and A. P. H. Trivelli, "Mathematical methods of frequency analysis of size of particles," J. Frank. Inst. **204**, 193–214, 377–389 (1927).

[3] J. C. Kapteyn and M. J. Van Uven, *Skew Frequency Curves in Biology and Statistics*, second paper (Groningen, 1916).

velli, reference 2.) The function (K) turned out to fit the observed size frequencies of some emulsions much better than (G), but it left in many cases considerable deviations which could not be abolished without retouching the formula and introducing further adjustable constants or parameters.

If we consider the function $f(x)$ as expressing a law of error, when the several x's stand for as many measurements of some quantity, then there is just as much justification for Kapteyn's as for Gauss's function. The Gaussian law of error gives for the most probable value of the quantity *the arithmetical mean* of its measurements which has always had a strong appeal as a just unique result of all those discrepant measurements. So also would a law of error of Kapteyn's form give for that most probable value *the geometrical mean* of the measurements which appeals equally to us or makes as substantial a claim to add to our knowledge as the arithmetical mean.[4] With equal right one might derive a law of error claiming the harmonic mean as the most probable value.

Returning to the actual meaning of x as the class size of a grain, we may consider both formulae, (G) and (K), as very special cases of

$$f(x)=f_m \exp\,(-[h(x)-h(x_m)]^2),$$

where $h(x)$ is some function of its argument, subject only to certain obvious, broad restrictions. Whatever abstract theory-of-error reasoning is applied to the size x itself, could as well be applied to the function h of the size x. If the numbers x were measurements of a quantity, the choice of the form of this function would, no doubt, be indicated by the manner of these measurements, and if these numbers stand for the sizes of grains or silver halide crystals, by the peculiarities of the actual formation and growth of the crystals. A convincing choice of the form of that function could thus be based only upon a quantitative theory of crystallization involving the solubility of grains of various sizes and other factors. Such a theory, in fact, would yield the complete distribution law, just as the kinetic theory of gases has led to the distribution of velocity or of kinetic energy among the molecules. But since we are far from possessing any such theory of crystallization, the only way left to us is to construct and to try out some reasonably simple empirical formulae.

The object of the present paper is to discuss such an empirical formula, differing not unessentially from (G) and (K), and to test it on several experimental size-frequency curves.

In deriving the formula in question, it has seemed most natural to start with the Gaussian form (G) and to amplify appropriately its exponent so as to secure in the first place, asymmetry and to do justice to other peculiarities of the actually observed size-frequency curves.

Let the exponent be written $\varphi(x)\cdot(x-x_m)^2$ and let, for computational convenience, the natural base e be replaced by 10, so that

$$f(x)=f_m\cdot 10^{-\varphi(x)(x-x_m)^2}, \qquad (2)$$

where $\varphi(x)$ is a function of x to be presently determined. Write, for brevity, $F=f/f_m$ and Log for $\log_{10}$. Then

$$\varphi(x)=-\mathrm{Log}\ F(x)/(x-x_m)^2.$$

Suppose that the constants x_m, f_m defining the peak of the curve have been chosen, say by interpolation between the two highest observed frequencies. Then the whole expression on the right-hand is observable, that is to say, can be evaluated for every class-size x. To begin with, let $\varphi(x)$ be just a short symbol for this expression. If the observed size-frequencies formed a normal or Gaussian set, $\varphi(x)$ would be a constant. Actually, however, such is by no means the case.

Now, having computed, for several emulsions, sets of φ values from the observed frequencies, I have noticed after the inspection of the corresponding φ, x curves and some numerical handling of the values of φ itself or of its logarithm, that, while $\varphi(x)$ changes considerably and systematically with x, its product into the square root of the absolute value of $x-\xi$ (where ξ is some constant) remains, at least within the most relevant x interval, nearly constant, say

$$\varphi(x)\cdot|x-\xi|^{\frac{1}{2}}=\kappa\doteqdot\text{constant}.^5$$

[4] As a matter of fact, a law of error identical with (K) was derived a long time ago by Sir Donald McAlister (Proc. Roy. Soc. **29**, 365 (1879)) from the requirement that it should lead to the *geometric mean* as the most probable value of the measured quantity.

[5] At first a fair approach to constancy has been achieved in a few cases by taking $|x-\xi|$ itself as a factor of φ, but the analysis of a larger experimental material has shown that $|x-\xi|^{\frac{1}{2}}$ as factor gives a much closer approximation to constancy.

The value of ξ, moreover, turned out to differ generally but little from the abscissa of the peak, $x=x_m$, of the size-frequency curve.

These empirical findings, then, have led us to consider for φ the form

$$\varphi(x)=\kappa/|x-\xi|^{\frac{1}{3}},$$

where κ is some positive constant and ξ another real constant whose sign need not be restricted a priori.

The resulting distribution function is, by (2),

$$f(x)=f_m\cdot 10^{-\kappa(x-x_m)^2/|x-\xi|^{\frac{1}{3}}}. \qquad (3)$$

This empirical formula has, so far, given fairly satisfactory results for a score or so of photographic emulsions differing as to the precipitation time and other details of their making.

Before giving the applications of the distribution function (3) to experimental size-frequency curves we may consider briefly its general properties.

Provided that $\xi\neq x_m$, the function $f(x)$ or the corresponding curve is manifestly asymmetrical with respect to its maximum ordinate erected at $x=x_m$. For so is the denominator of the exponent. If ξ were equal to x_m (which actually will never be the case), the exponent would reduce to $-\kappa|x-x_m|^{\frac{1}{3}}$ and the curve (3) would become symmetrical, though still differing in shape from the normal curve. It would degenerate into the normal or Gaussian curve only if $|\xi|$ were enormous in comparison with all contemplated grain sizes; for the exponent would then be proportional to $(x-x_m)^2$ itself. If ξ were negative, the point $x=\xi$ would of course fall outside the limits of the physical applicability of the formula. As a matter of fact, the parameter ξ is neither negative nor enormous, but positive and comparable in value with x_m, though perceptibly different from x_m. In fine, the point $x=\xi$ has turned out to lie within the most relevant interval of the experimental sizes, and cannot thus be disregarded. Now, for $x=\xi\neq x_m$, the exponent in (3) becomes negatively infinite, so that

$$f(\xi)=0,$$

indicating the non-existence of grains of just the size ξ. (But so also is the number of grains of "just" any other size x equal to nil.) In other words, the curve (3) forms in the neighborhood of ξ a precipitous wedge plunging down to the x axis.

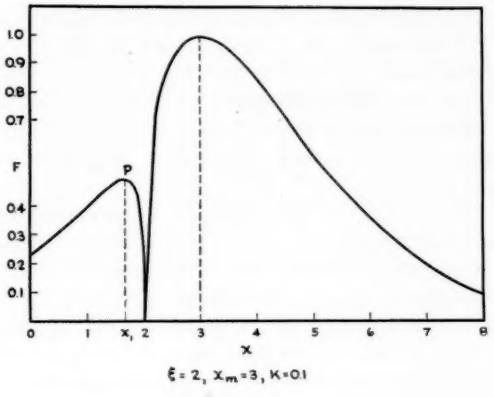


FIG. 1.

The number of grains of mean class-size ξ, however, has some finite value, namely,

$$\int_{\xi-\Delta/2}^{\xi+\Delta/2} f(x)dx,$$

which may or may not be much smaller than the frequencies of the two neighbor classes. This will depend upon the proximity of ξ to x_m, the position of the main peak f_m of the curve. In order to give an idea of this peculiarity, the curve (3), with $F=f/f_m$ as ordinate, is drawn in all detail in the neighborhood of $x=\xi$ for the case $\kappa=0.1$, $\xi=2$, $x_m=3$, in Fig. 1. The abscissa of the secondary, spurious peak P is easily found to be

$$x_1=\tfrac{1}{3}(4\xi-x_m);$$

in the present case, $x_1=5/3$; the corresponding ordinate, always smaller than $F_m=1$, is $F_1=0.492$. The wedge reaching down to $F=0$ at $x=\xi=2$ is, comparatively, very narrow. We may mention that in all practical applications so far made of formula (3) the mean width of this wedge amounts only to a fraction of the usual class width, and since the latter cannot even be halved, for technical reasons, the existence of this wedge as a peculiarity of our distribution function remains so far a purely formal affair which can be neither contradicted nor confirmed by experiment. On the other hand, this for the present superfluous peculiarity of the function $f(x)$ may, perhaps, in the future turn out to correspond or to serve as a hint to some physical peculiarity of the crystallization process, as, e.g., the instability of crystals of a certain size ξ. According to Mr.

Trivelli some substantial and rather sudden changes in the shape and the solubility of the AgBr crystals occur not far from the observable peak (x_m) and in a few cases were actually located within the limits of our theoretical wedge. These changes consist, visually, in a sudden passage from round to hexagonal crystals between a certain class and the next higher size-class. In one case, for instance, in which the observed size-frequency curve was closely represented by our function with $x_m=0.35$ and $\xi=0.40\mu^2$ (midpoint and upper limit of the fourth class) and thus with the wedge extending to about $0.45\mu^2$ (midpoint of the fifth class), the grains up to and within the third class were almost all round, half of those of the fourth class were round and half hexagonal, and those of the fifth class, all hexagonal. This marked change, then, occurred just within the wedge. Similar coincidences could be noted in a few other cases.

These few, scattered observations do not, however, enable us to make any positive statements or to clinch the question whether the said peculiarity of the distribution function (3) is purely mathematical, and thus superfluous, or corresponds to some actual feature of the precipitation process. For the present, at least, we must be content to consider (3) merely as an empirical formula capable of giving a fairly close representation of the observed size-frequencies.

We shall now pass to testing the experimental size-frequencies found in these Laboratories for several photographic emulsions. It will suffice to refer to these emulsions, conventionally, by Roman numerals.

For numerical computations it will be expedient to use as our independent variable

$$x=20\times\text{mean class-size in }\mu^2,$$

so that the first and the consecutive classes will be specified by the integers 1, 3, 5, and so on.

EMULSION I

Mean grain size $\bar{a}=0.284\mu^2$, standard deviation $\sigma=0.164\mu^2$. Total number of grains counted, in 14 classes, $n=1003$. The first four classes were found to contain the following numbers (f) of grains:

$x=1$	3	5	7
$f=56$	292	272	203.

Having assumed, after a few trials,

$$f_m=300 \text{ at } x_m=4,$$

we find from these observed frequencies the following values of $-\text{Log } F=\text{Log } (f_m/f)$ and $\varphi(x)=-\text{Log } F/(x-x_m)^2$:

$x=1$	3	5	7
$-\text{Log } F=0.729$	0.012	0.036	0.170
$\varphi(x)=0.081$	0.012	0.036	0.019.

In order to represent these $\varphi(x)$ values by $\kappa|x-\xi|^{-\frac{1}{2}}$ let us try to determine the coefficients κ, ξ from $\varphi(1)$ and $\varphi(7)$. If we assume, tentatively, that $1<\xi<7$, the two equations are $\kappa^2/(\xi-1)=\varphi^2(1)$ and $\kappa^2/(7-\xi)=\varphi^2(7)$, whence

$$\xi=1.31, \qquad \kappa=0.0452.$$

Thus, the formula (3) becomes

$$\text{Log } (f/300)=-0.0452(x-4)^2/|x-1.31|^{\frac{1}{2}}.$$

This gives the following results:

$x=$	1	3	(4)	5	7	9	11	13	15	17	19	21	23	25	27
$f=$	56	277	300	284	203	117	59	26	10	3.5	1.1	0.34	0.08	.02	.006
$f_{obs}=$	56	292±10	—	276±9.5	203	83±6	43±4	29	11	4	1	2	0	2	1

The last line gives the numbers actually counted with some of their p.e. computed by formula (1). The agreement between the calculated and the observed frequencies is, perhaps with the exception of $f(9)$, close enough. The corresponding diagram, with abscissae in μ^2 (and thus $x/20$), is given in Fig. 2, where a smooth curve has been drawn through the calculated points $x=1$, 3, 4, 5, 7, etc., with the omission of the narrow "wedge" whose center, marked by V, falls near the midpoint of the first class, at $0.066\mu^2$. The observed frequencies are marked by eyelets.

EMULSION II

$\bar{a}=0.151$, $\sigma=0.122\mu^2$. Total number of grains counted, in 9 classes,

$$n=1035.$$

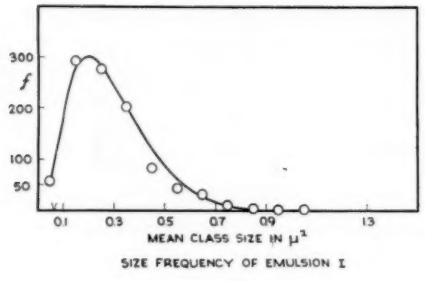


FIG. 2.

In this case, however, f stands for frequency per 1000. The two highest frequencies observed being $f(1)=401$ and $f(3)=367$, we have taken

$$f_m=425, \quad \text{at} \quad x_m=2.$$

In a first trial the coefficients ξ, κ were determined, by a process explained above, from $\varphi(1)$ and $\varphi(5)$. The resulting curve (3), however, has shown a much too slow descent beyond x_m. When these constants are determined from $\varphi(3)$ and $\varphi(7)$ instead, their values are $\xi=3.94$, $\kappa=0.0621$, and the resultant formula becomes

$$\text{Log}\,(f/425)=-0.0621(x-2)^2/|x-3.94|^{\frac{1}{2}}.$$

It gives, for the nine classes investigated, the following results:

$x=$	1	(2)	3	5	7	9	11	13	15	17
$f(x)=$	391	425	367	122	55	19	5.5	1.4	0.30	0.06
$f_{\text{obs}}=$	401 ± 10	—	367	134 ± 7	55	23 ± 3	7.7 ± 1.8	4.8 ± 1.5	3.9 ± 1.4	2.9 ± 1.3

The corresponding graph is given in Fig. 3; the wedge, marked as before, is now placed beyond the peak of the curve. The agreement of the calculated with the observed frequencies is close enough, at least up to the seventh class.

EMULSION III

$\bar{a}=0.179$, $\sigma=0.138\mu^2$. Total number of grains counted, in 12 classes,

$$n=1010.$$

The f_{obs} values quoted below are the unreduced numbers of grains counted in each class.

Rounding off the curve between the two highest observed frequencies, $f(1)=300$ and $f(3)=396$, the coordinates $f_m=425$, $x_m=2$ have been assumed for the peak of the curve. After a few trials the best values of the remaining two parameters turned out to be those derivable from $\varphi(1)$ and $\varphi(7)$. They are $\xi=1.21$ and $\kappa=0.070$. Thus, the formula (3) becomes

$$\text{Log}\,(f/425)=-0.070(x-2)^2/|x-1.21|^{\frac{1}{2}}.$$

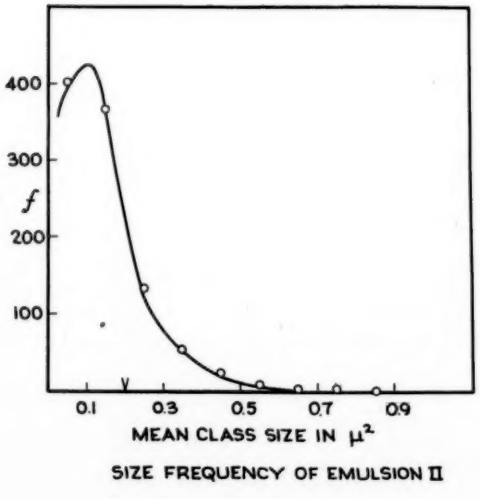


FIG. 3.

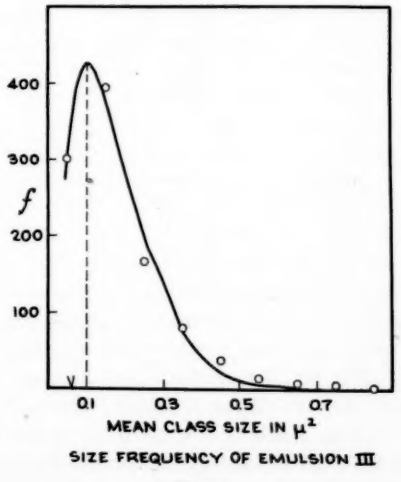


FIG. 4.

Its comparison with the observed frequencies is as follows:

$x=$	1	(2)	3	5	7	9	11	13	15	17	19	21	23
$f(x)=$	300	425	377	202	80	25	6.6	1.5	0.28	—	0.007	—	—
$f_{obs}=$	300	—	396±10	166±8	80	39	13±2.4	8	4	1	0	2	1

The differences are greater than in the preceding cases, but still tolerable. The corresponding graph, Fig. 4, shows, on the whole, a sufficiently close agreement with the observed points, marked by eyelets.

EMULSION IV

$\bar{a}=0.314$, $\sigma=0.226\mu^2$. Total number of grains counted in (nominally 16, but practically only) 11 classes,

$$n=2819.$$

The frequencies were reduced to a total of 1000. The mean class sizes are here twice the usual ones, i.e., 0.1, 0.3, $0.5\mu^2$, etc. To retain, therefore, our previous x values, 1, 3, 5, etc., for the classes, x is in this particular case given the meaning of 10 times the class size in μ^2. The observed frequencies $f(x)$, per 1000, in the first three classes are $f(1)=353, f(3)=406, f(5)=155$. Having assumed, after some trials, $f_m=450$, at $x_m=2$, one finds from $\varphi(1)$ and $\varphi(5)$ the parameters $\xi=1.773$, $\kappa=0.0923$. Thus, and retaining but three significant figures, the distribution formula (3) becomes

$$\text{Log}\,(f/450)=-0.0923(x-2)^2/|x-1.77|^{\frac{1}{2}}.$$

This gives a fairly close representation of the actual frequencies for the first six classes. The higher classes contain but too sporadic grains to be of any importance. The corresponding graph, Fig. 5, will show that the observed size-frequency distribution is essentially well reproduced.

EMULSION V

$\bar{a}=0.271$, $\sigma=0.171\mu^2$. Total number of grains counted,

$$n=\Sigma f=717$$

in fourteen classes of the usual mean class size. Since the last three classes contain only sporadic grains, *viz.*, 2, 0, 1, we shall quote below only the findings for the first eleven classes. In view of the comparatively excellent regularity of the observed frequencies, this set of data has been analyzed with particular care.

The two highest observed frequencies (unreduced) being $f(3)=230$ and $f(5)=208$, the peak of the curve has, after some trials, been placed at

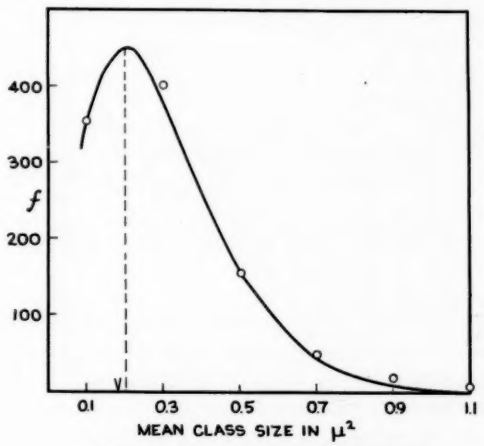
$$x_m=3.50, \qquad f_m=235.$$

A first determination of the remaining two parameters from $\varphi(1)$ and $\varphi(5)$ having given a curve of too slow descent beyond the peak, these parameters have ultimately been determined from $\varphi(1)$ and $\varphi(7)$, in a manner explained in the first example. Their values thus found are

$$\xi=1.31, \qquad \kappa=0.0596,$$

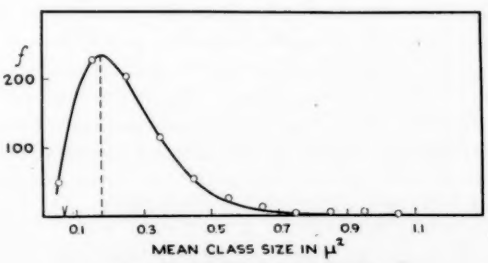
so that the formula (3) becomes

$$\text{Log}\,(f(x)/235)=-0.0596(x-3.50)^2/|x-1.31|^{\frac{1}{2}}.$$



SIZE FREQUENCY OF EMULSION IV

FIG. 5.



SIZE FREQUENCY OF EMULSION V

FIG. 6.

This formula gives for the aforesaid eleven classes the following results:

$x=1$	3	(3.50)	5	7	9	11	13	15	17	19	21
$f(x)=50$	229	235	200	115	53	20	6.3	2.1	0.42	0.40	0.39
$f_{obs}=50$	230	—	208 ± 8.2	115	58 ± 5	25 ± 3.3	12 ± 2	3	6	6	1

The agreement is very close throughout (apart from the erratic two sixes in the tail). A graphical representation of these results is given in Fig. 6, with the same meaning of symbols or marks as before.

These examples, with a number of other equally satisfactory ones not included here, will suffice, perhaps, to show that the proposed formula (3) is capable of giving a fair representation of the distribution of size frequencies in photographic emulsions. The possible physical peculiarities of precipitates corresponding to the narrow wedge implied by the divisor $|x-\xi|^{\frac{1}{2}}$ of the exponent are now under investigation. In the meantime no definite physical meaning, apart from the vague interpretation given above, can be claimed for the vanishing of the proposed distribution function at $x=\xi$.

JANUARY, 1943 J. O. S. A. VOLUME 33

Propagation of Radiation in a Scattering and Absorbing Medium

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(Received October 17, 1942)

It is assumed that collimated radiation i_0 and diffuse radiation a_0 are incident on the upper surface of a horizontal slab of a medium which scatters and absorbs the radiation. The slab is infinite in horizontal directions and of thickness t in the vertical direction; r is the reflectivity of the lower surface. Equations are derived for a and b, where at a distance x below the upper surface a and b are the streams of radiation flowing downward and upward, respectively. With appropriate assumptions the equations are reduced to relations that refer to the optics of the sea and the sky.

SEVERAL cases of the optical properties of absorbing, scattering, and emitting media have received theoretical attention, such as the luminous atmosphere of a star,[1] the diffusion of light in a cloud,[2] the thermal state of the terrestrial atmosphere,[3] and opal glasses and paints.[4] In the present paper the theory of the passage of light in a medium that scatters and absorbs is developed with special boundary conditions for application to the cases of the sea and the sky.

A medium is assumed that absorbs and scatters radiation. We shall deal with collimated, or parallel-ray, radiation and with diffuse radiation, or radiation for which the energy flow is the same in all directions. For monochromatic radiation the attenuation coefficients of the medium due to absorption are denoted by β_c and β_d for collimated and diffuse radiation, respectively, and the respective attenuation coefficients due to scattering are denoted by σ_c and σ_d. The fractions $\eta_c\sigma_c$ and $(1-\eta_c)\sigma_c$ of the collimated radiation and $\eta_d\sigma_d$ and $(1-\eta_d)\sigma_d$ of the diffuse radiation are scattered in the forward and backward directions, respectively.

In general, β_c, σ_c, and η_c are not equal, respectively, to β_d, β_d, and η_d. In particular, the attenuation of diffuse radiation passing through a thin layer of the medium is twice the attenuation of collimated radiation passing normally through the thin layer. This is well known, but the proof may be recalled here. It is as follows:

[1] A. Schuster, Astrophys. J. **21**, 1–22 (1905).
[2] I. Langmuir and W. F. Westendorp, Physics **1**, 273–317 (1931).
[3] E. O. Hulburt, Phys. Rev. **38**, 1876–1890 (1931).
[4] An excellent list of references is given by S. Q. Duntley, J. Opt. Soc. Am. **32**, 61–70 (1942).

Consider a unit area of the medium of thickness dx. If F_c is a flux of collimated radiation incident normally on the area and α_c is the attenuation coefficient for collimated radiation, due to absorption or to scattering or to other causes, the reduction in F_c in passing through the area is ΔF_c, where, by definition of α_c,

$$\Delta F_c = F_c \alpha_c dx. \tag{1}$$

Similarly, if F_d is a flux of diffuse radiation incident on the area and α_d is the attenuation coefficient for diffuse radiation, the reduction in F_d in passing through the area is ΔF_d, where, by definition of α_d,

$$\Delta F_d = F_d \alpha_d dx. \tag{2}$$

Now F_d is a total flux which is composed of f_d, a flux density per unit solid angle which is the same in all directions. Let ϕ be the angle between f_d and the normal to the unit area. Then

$$F_d = f_d \int_0^{\pi/2} 2\pi \sin \phi \cos \phi d\phi = \pi f_d. \tag{3}$$

f_d is reduced by an amount $f_d \alpha_c \sec \phi dx$ in passing through thickness dx in the direction ϕ, as seen from (1). Therefore

$$\Delta F_d = f_d \int_0^{\pi/2} 2\pi \alpha_c \sin \phi d\phi dx = 2\pi f_d \alpha_c dx,$$

and from (3)

$$\Delta F_d = 2F_d \alpha_c dx. \tag{4}$$

Comparing (2) and (4) it is seen that $\alpha_d = 2\alpha_c$. Therefore

$$\beta_d = 2\beta_c \quad \text{and} \quad \sigma_d = 2\sigma_c. \tag{5}$$

It is true, of course, that (5) is correct only for the uniformly diffuse radiation considered in the preceding paragraphs, and that in general after the radiation has passed through the attenuating layer it is no longer uniformly diffuse. The effect is brought out in the well-known calculation of Gold,[5] from which it follows that as diffuse radiation progresses into an attenuating medium, the attenuation coefficient at first is $2\alpha_c$ and descends toward the value α_c. This is due to the fact that the distribution of the diffuse radiation, which at first is uniform over a hemisphere, becomes restricted to a cone whose angular diameter decreases as the distance into the medium increases, until finally the cone is so small that the radiation is practically collimated.

In the following analysis the assumption is made that the diffuse radiation is of the same type of diffuseness throughout the medium. This means that β_d, σ_d, and η_d are assumed to be constant throughout the medium. Since cases may occur for which the assumption is not true, one must be careful in applying the present results to such cases. A more exact analysis would calculate the type of diffuseness at all points in the medium. This appears intricate and is not attempted here.

The scattering and absorbing medium is assumed to be infinite in the horizontal direction, and to be bounded by upper and lower surfaces that are plane and horizontal, and a distance t apart in the vertical direction. The lower surface is diffusely reflecting of reflectivity r. Passing into the upper surface of the medium are two types of monochromatic radiation, one diffuse of flux density a_0, and the other collimated of flux density i_0. The direction of i_0 is at angle ζ with the vertical. In general η_c is a function of ζ. In the course of their passage through the medium the radiations are absorbed and are scattered upward and downward, thereby giving rise to two streams of diffuse radiation, one stream a moving downward and one stream b moving upward. Radiation that reaches the lower surface is reflected back into the medium and contributes to the a and b streams. In the following paragraphs these ideas are expressed mathematically and equations are obtained by assuming optical equilibrium and equating the amount of radiation flowing into any horizontal layer of the medium to the amount flowing out of the layer. This is the method of Schuster.[1]

In Fig. 1 is shown a vertical section of the medium and of a horizontal thin layer of thickness dx situated a distance x below the upper surface. Let the subscripts o, no subscript, and t refer to the upper surface, the layer, and the lower surface, respectively. Then for the collimated radiation

$$i = i_0 \exp\left[-(\beta_c + \sigma_c) \sec \zeta \cdot x\right], \tag{6}$$

$$i_t = i_0 \exp\left[-(\beta_c + \sigma_c) \sec \zeta \cdot t\right]. \tag{7}$$

[5] E. Gold, Proc. Roy. Soc. **82**, 43–70 (1909).

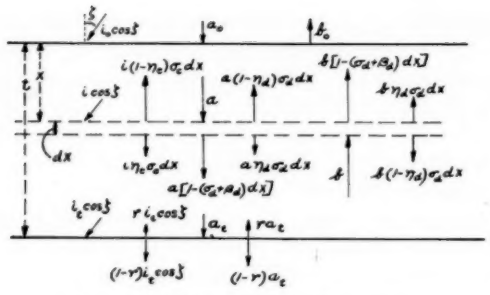

FIG. 1. Scattering and absorption process.

The flux entering unit area of the layer is $i\cos\zeta$, and of this an amount $i\cos\zeta\cdot(\beta_c+\sigma_c)dx\cdot\sec\zeta=i\beta_c dx+i\sigma_c dx$ is removed by the layer. The first term is due to absorption, the energy being converted into heat. The second term is the scattered radiation; an amount $i\eta_c\sigma_c dx$ is scattered downward and contributes to the a stream, and an amount $i(1-\eta_c)\sigma_c dx$ is scattered upward and contributes to the b stream—similarly for the a and b streams in their passage through the layer. The details of the various processes are shown in Fig. 1. Then, referring to Fig. 1,

$$da=a[1-(\beta_d+\sigma_d)dx]+a\eta_d\sigma_d dx+b(1-\eta_d)\sigma_d dx+i\eta_c\sigma_c dx-a, \quad (8)$$

$$db=b-b[1-(\beta_d+\sigma_d)dx]-b\eta_d\sigma_d dx-a(1-\eta_d)\sigma_d dx-i(1-\eta_c)\sigma_c dx, \quad (9)$$

which reduce to

$$da/dx=(-a+b)(1-\eta_d)\sigma_d+i\eta_c\sigma_c-a\beta_d, \quad (10)$$

$$db/dx=(-a+b)(1-\eta_d)\sigma_d-i(1-\eta_c)\sigma_c+b\beta_d. \quad (11)$$

Equating the radiation entering and leaving the medium yields

$$a_0+i_0\cos\zeta=b_0+(1-r)(a_t+i_t\cos\zeta). \quad (12)$$

Solving (10) and (11), and introducing (6), (7), and (12) leads to

$$a=(\sinh\gamma t)^{-1}\{a_0\sinh\gamma(t-x)+a_t\sinh\gamma x+I_0C[\sinh\gamma(t-x)-X\sinh\gamma t+T\sinh\gamma x]\}, \quad (13)$$

$$a_t=[\gamma a_0+I_0\{\gamma C-T[(CA-B\sec\zeta+g)\times\sinh\gamma t+C\gamma\cosh\gamma t]\}]\times\{(g+\beta_d)\sinh\gamma t+\gamma\cosh\gamma t\}^{-1}, \quad (14)$$

$$b=(\sinh\gamma t)^{-1}\{b_0\sinh\gamma(t-x)+b_t\sinh\gamma x+I_0D[\sinh\gamma(t-x)-X\sinh\gamma t+T\sinh\gamma x]\}, \quad (15)$$

$$b_0=\{[a_0(1-\eta_d)\sigma_d+i_0(1-\eta_c)\sigma_c]\sinh\gamma t+\gamma b_t-I_0D(\gamma\cosh\gamma t-A\sinh\gamma t-\gamma T)\}\times\{\gamma\cosh\gamma t+[(1-\eta_d)\sigma_d+\beta_d]\times\sinh\gamma t\}^{-1}, \quad (16)$$

$$b_t=r[\gamma a_0+I_0\{\gamma C-T[(CA-B\sec\zeta-\beta_d)\times\sinh\gamma t+(C-1)\gamma\cosh\gamma t]\}]\times\{(g+\beta_d)\sinh\gamma t+\gamma\cosh\gamma t\}^{-1}, \quad (17)$$

where

$$I_0=i_0\cos\zeta,$$
$$\gamma=\{\beta_d[2(1-\eta_d)\sigma_d+\beta_d]\}^{\frac{1}{2}},$$
$$g=(1-r)(1-\eta_d)\sigma_d,$$
$$X=e^{-Ax},$$
$$T=e^{-At},$$
$$A=(\beta_c+\sigma_c)\sec\zeta,$$
$$B=\eta_c\sigma_c+(1-\eta_d)\sigma_d\cos\zeta,$$
$$C=\sigma_c[\eta_c(\beta_d\cos\zeta+\beta_c+\sigma_c)+(1-\eta_d)\sigma_d\cos\zeta]\times[(\beta_c+\sigma_c)^2-\gamma^2\cos^2\zeta]^{-1},$$
$$D=\sigma_c[(1-\eta_c)(\beta_d\cos\zeta-\beta_c-\sigma_c)+(1-\eta_d)\sigma_d\cos\zeta]\times[(\beta_c+\sigma_c)^2-\gamma^2\cos^2\zeta]^{-1}.$$

The algebraic details of the solutions are elementary and are too long to be given here. In general, i_0, a_0, β_d, β_c, σ_d, σ_c, η_c, η_d, and r are functions of the wave-length λ. If these quantities and x and t are known, a, a_t, b, b_0, and b_t may be calculated from Eqs. (13) to (17). This constitutes the solution of the problem proposed in this paper.

To obtain the simple case of diffuse radiation in a scattering medium set $i_0=\beta_c=\beta_d=r=0$. Equations (13) and (15) reduce to

$$a=a_0\frac{1+\sigma_d(1-\eta_d)(t-x)}{1+(1-\eta_d)\sigma_d t}, \quad (18)$$

$$b=a_0\frac{\sigma_d(1-\eta_d)(t-x)}{1+(1-\eta_d)\sigma_d t}. \quad (19)$$

With $\eta_d=\frac{1}{2}$, (18) and (19) become

$$a=a_0\frac{1+\sigma_d(t-x)/2}{1+\sigma_d t/2}, \quad (20)$$

$$b=a_0\frac{\sigma_d(t-x)/2}{1+\sigma_d t/2}. \quad (21)$$

Equations (20) and (21) are the same as the

equations of Schuster.[6] They are true only in the case that σ_d is constant with x, or in other words, that the diffuse radiation is diffuse throughout the medium.

THE CASE OF THE ATMOSPHERE

In the case of the terrestrial atmosphere below the ozone region β is approximately zero for the wave-lengths of the visible spectrum. During daylight i_0 is the light of the sun that falls on the "top" of the atmosphere, and a_0 is approximately zero. If t is the optical thickness of the atmosphere, a is related to the average brightness of the daylight sky to an observer looking upward from a point at an optical distance x below the top, and a_t to the average sky brightness seen by an observer on the surface of the earth. b_0 is related to the average brightness of the atmosphere seen by an observer above the atmosphere looking downward.

With $\beta_c=\beta_d=0$, Eqs. (13) to (17) reduce, respectively, to

$$a=I_0(1+gt)^{-1}\{(1+gt)(C-CX) -gx(C-CT+T)\}, \quad (22)$$

$$a_t=I_0(1+gt)^{-1}(C-CT-gtT), \quad (23)$$

$$b=I_0(1+gt)^{-1}\{(1+gt)(C-CX+X) -(gx+1-r)(C-CT+T)\}, \quad (24)$$

$$b_0=I_0(1+gt)^{-1} \times\{(1+gt)-(1-r)(C-CT+T)\}, \quad (25)$$

$$b_t=I_0r(1+gt)^{-1}(C-CT+T), \quad (26)$$

[6] A. Schuster and J. W. Nicholson, *The Theory of Optics* (Longmans, Green and Company, 1924), third edition, page 271.

where

$$\begin{aligned} I_0&=i_0\cos\zeta,\\ g&=(1-r)(1-\eta_d)\sigma_d,\\ C&=\eta_c+(1-\eta_d)(\sigma_d/\sigma_e)\cos\zeta,\\ X&=\exp(-\sigma_e\sec\zeta\cdot x),\\ T&=\exp(-\sigma_e\sec\zeta\cdot t). \end{aligned} \quad (27)$$

Equations (22) to (27) comprise part of a detailed theory of the brightness and polarization of all points of the daylight sky viewed by an observer at various altitudes above the earth. The detailed theory and comparison with observations will be given in a future paper.

THE CASE OF THE DEEP SEA

In the case of the sea i_0 and a_0 are the light of the sun and the sky, respectively, that enter the surface of the sea. For light of the visible spectrum both absorption and scattering are important, and Eqs. (13) to (17) apply directly to a sea of finite depth and take into account the reflectivity of the bottom. For an infinitely deep sea, that is, a sea so deep that the amount of light penetrating to the lower levels is negligible, $t=\infty$ and $a_t=b_t=0$.

With $t=\infty$, Eqs. (13), (15), and (16) reduce, respectively, to

$$a=a_0e^{-\gamma x}+I_0C(e^{-\gamma x}-X), \quad (28)$$

$$b=b_0e^{-\gamma x}+I_0D(e^{-\gamma x}-X), \quad (29)$$

$$b_0=[a_0(1-\eta_d)\sigma_d+i_0(1-\eta_c)\sigma_e-I_0D(\gamma-A)] \times[\beta_d+(1-\eta_d)\sigma_d+\gamma]^{-1}. \quad (30)$$

The application of these equations to optical measurements of the sea will be given in a future paper.

JANUARY, 1943 J. O. S. A. VOLUME 33

Electronic Voltage Regulator for Precise Densitometric Measurements*

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IT is a well-known fact that the precision of densitometric measurements, and thus the precision of quantitative spectrochemical determinations, is dependent upon the constancy of illumination of the densitometer lamp. The problem of maintaining this constancy proves to be a very difficult one, as to maintain the light output accurate to ±0.2 percent demands voltage control accurate to about ±0.07 percent.

In reading the advertising literature on voltage regulators, this does not seem particularly diffi-

* Presented at the Tenth Summer Conference on Spectroscopy and its Applications held at the Massachusetts Institute of Technology, Cambridge, Massachusetts, July 20–22, 1942.

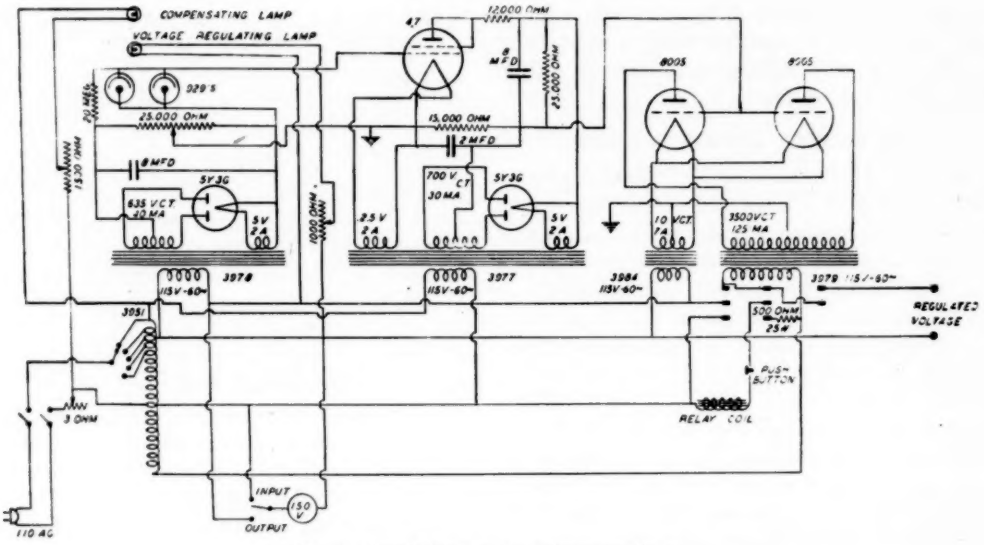

FIG. 1. Circuit diagram for voltage regulator.

cult however, as there are on the market several simple regulators of the resonance transformer type, or the saturated core type, which claim to limit the output variation to one volt for an input variation from 90 volts to 130 volts. This indicates a degree of correction of at least twenty to forty depending upon the shape of the output *vs.* input curve. If we assume a factor of thirty, this limits a ± 3-volt change at the input to ± 0.1 percent at the output. This would be almost good enough for accurate densitometric measurements for this degree of input change and would certainly suffice when ordinarily uniform line voltage was available.

However, the difficulty with this type of regulator proves not to be related to the obvious thing, change of input voltage, but rather to a less well-known thing, change of input frequency. For instance, one well-known make of regulator will vary its output voltage by 1.6 volts for a 1 percent change in input frequency. The question then arises what variation in frequency can be expected in the usual commercial power installation. In general, the newer power installations are giving considerable attention to frequency stabilization. Probably the best one in this respect is the new installation at Boulder Dam, in which the frequency is never allowed to drift by more than 0.1 cycle in 60 cycles. However, in the small power plants supplying some municipalities, the drift in frequency may amount to as much as 0.5 cycle in 60 cycles. On the average, of course, the output is made exactly 60 cycles, so that such power can be used to operate clocks and other synchronous devices. Thus, merely because a power company advertises that electric clocks may be used is no assurance that frequency variations do not occur. With these facts in mind, what voltage variations can then be expected? In cases of excellent frequency stabilization, 0.1 cycle in 60, this amounts to a variation of 0.26 percent in output voltage which, transposed into transmission readings, can cause variations of almost 0.8 percent. In cases of a 0.5 cycle variation, fluctuation of 5 percent can be expected in transmission readings on the densitometer.

This state of affairs has led many people using and building densitometers to the conclusion that something as stable as a large capacity storage battery floating across a charging line is the only really good solution to this problem. However, anyone who has used an instrument powered by alternating current, which has worked reasonably well, is very reluctant to accept this solution and will only do so as a last resort.

From the above discussion it seems that the

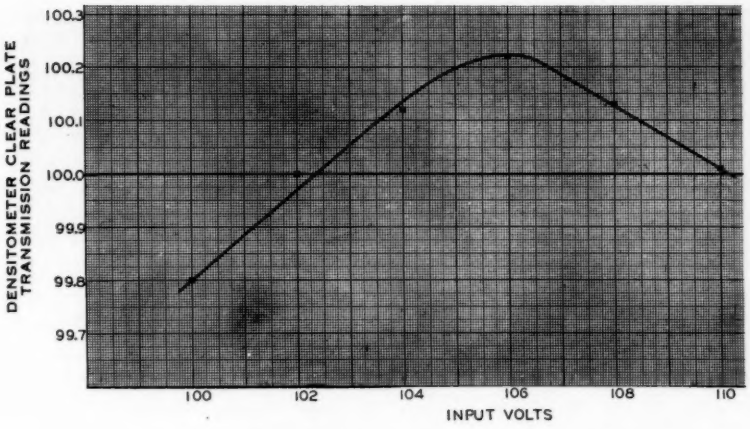

FIG. 2. Variations in clear plate transmission readings as a function of input voltage to regulator.

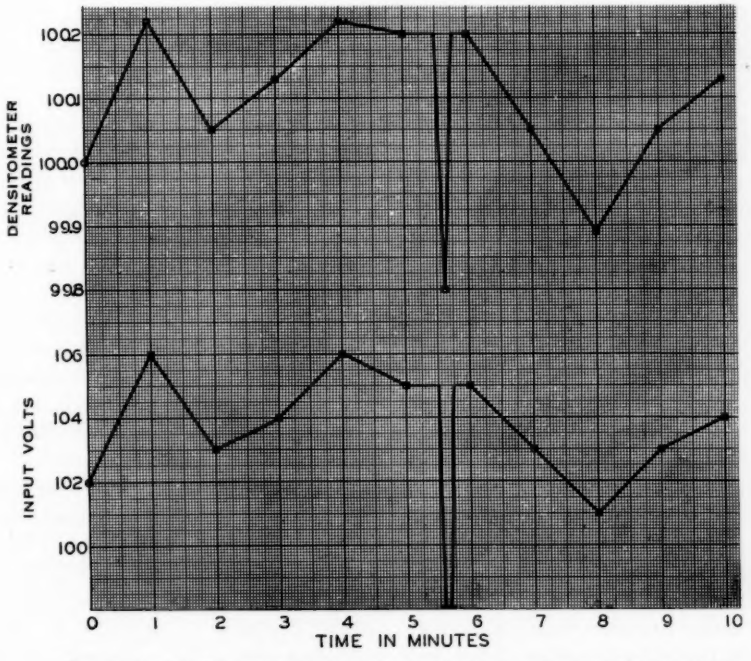

FIG. 3. A typical example of the variations in input voltage and the resultant variations in densitometer readings experienced in a ten-minute period of operation.

best mode of attack on the problem is to devise a regulator that is independent of frequency variations.

Since the voltage output of an ordinary well-designed transformer is independent of frequency variations to a first approximation, the most fruitful mode of attack appears to be to use two regular transformers in series, the first one raising the input voltage a certain amount above that desired, and the second one dropping that excess

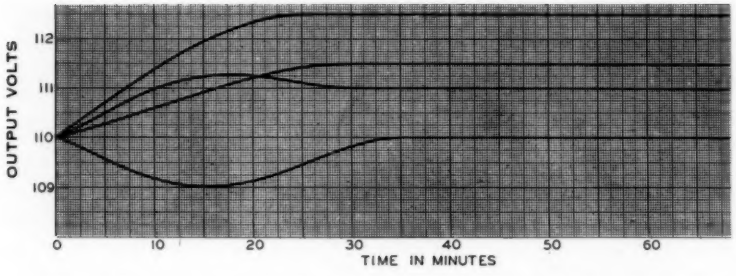

FIG. 4. Change of output voltage experienced from four different regulators during the warm-up period.

voltage in varying amounts so that the final output remains constant at the desired value. Such a device furnishes alternating current in the output, which is very desirable, as the same regulator that furnishes constant voltage to the densitometer lamp may then be used to power the densitometer amplifier, if such is required. For most other commercial uses to which a regulator may be applied, an alternating current output is, of course, almost a necessity.

The arrangement finally adopted is shown in the circuit diagram, Fig. 1. Transformer *3951* raises the input voltage from 115 v to about 200 v, while transformer *3979* drops the output voltage back to 110 v. The two amplifier tubes across the output of this transformer act as a variable resistance load, and thus by controlling the grids of these tubes in a compensating manner, exact control of the voltage may be obtained. By operating these tubes at the correct grid bias, almost a linear change of current with change of voltage is obtained, so that they act very much as a pure resistance. In this manner very little distortion of wave form is introduced. Gaseous tubes, such as thyratrons, would, of course, give a large distortion of wave form.

The method of controlling the grids of these amplifier tubes proves particularly suitable to the problem in hand. Lights with fine filaments, and hence with low thermal inertia, are used as the controlling elements. In this way an integrated correction, independent of exact wave form, frequency, or voltage, is obtained, which tends to keep the densitometer lamp very constant. The correction has been applied in two ways, first, as a compensating effect, and second, as a regulating effect. By adjusting the position and intensity of the lamp connected to the input voltage, compensation of almost all variations can be achieved by means of the photo-cells and the vacuum tube amplifier feeding into the grids of the amplifier. However, use of just this control proves not to be sufficient, as it suffers from the usual limitation attendant in all compensating circuits, namely, perfect compensation at only one input voltage. Thus, a second lamp is used, operating from the output voltage, which has a true regulating effect—the ability to reduce any change to a small fraction of itself. This lamp alone will reduce a 10-volt change to about 1 volt, and when used in conjunction with the compensating lamp, gives a very stable output voltage.

Just how stable this can be is shown in Fig. 2 where the output of a linear densitometer is given as a function of input voltage. These results appear very acceptable and show that for a ± 5-volt change, the transmission readings will vary by about ± 0.2 percent. Results over a period of ten minutes, shown in Fig. 3 indicate the degree of constancy that can be expected in regular operation. Surges, one of which is shown in the last mentioned figure, are noticeable if they are large enough, but thanks to the low thermal inertia of the controlling lamp and the high thermal inertia of the densitometer lamp, they do not introduce appreciable errors.

Besides the ability to compensate at any one time, a regulator must also be able to maintain its output constant over reasonably long periods of time—ten minutes to a half hour—while a single plate or film is read in its entirety. This presented quite a problem, due to the large power requirements of the ARL-Dietert comparator-

densitometer for which the unit was designed. It had to be able to supply 160 watts of extremely well-regulated power, which necessitated an input of between 400 and 500 watts, and a dissipation of almost 300 watts. The dissipation of this much power causes a considerable rise in temperature of the component parts of the regulator, which, in turn, causes an initial drift in output voltage until approximate thermal equilibrium is reached. This takes from fifteen to thirty minutes, after which the regulator maintains its output voltage very accurately over long periods. Figure 4 shows this initial drift and subsequent stabilization for four different regulators. The differences between units can doubtlessly be attributed to different temperature coefficients for the different component parts. The part most sensitive to temperature changes proved to be the 20-meg. resistor in the photo-tube circuit. Experiments extending over many months indicated that a slow, continued change could be experienced with certain makes of resistors over many hours. This, of course, caused undesirable drifting. However, two 10-meg. G.H. resistors proved most successful in avoiding this effect. Since employing these resistors, very stable operation is experienced after the warm-up period. This period has been reduced in time in the new models by ventilating the whole unit more effectively than was done in the older models.

JANUARY, 1943 J. O. S. A. VOLUME 33

Preparation of Purified Inorganic Compounds for Use in Spectrographic Standards*

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THE lack of sufficiently pure chemicals for use in the preparation of standard samples required for comparison purposes, or for the establishment of working curves, often determines the lower limit at which spectrographic analyses may be made with the desired accuracy. Available chemicals, even those of the highest purity obtainable, may be unsatisfactory for certain purposes. The need for materials of high purity for use in the analysis of metals and alloys has been recognized by the American Society for Testing Materials,[1,2] and a survey of sources of "super-purity" metals has been made.[3] A similar need exists for compounds of high purity for use in preparing standards for spectrographic analysis of agricultural samples. Since satisfactory chemicals are not obtainable, it has been necessary to prepare materials suitable for the proposed use by removal of objectionable impurities from the available chemicals. The need for purified compounds for spectrographic use, and the obvious applications of purified chemicals to other problems, was considered to justify a description of some methods which have been found useful for the preparation of compounds of the required purity.

Published information on methods for the preparation of purified chemicals is widely scattered and difficult to assemble, since most of it has been published as a part of researches in which the preparation of purified compounds was not the primary object; consequently, these publications have often been abstracted and indexed with little regard for purification problems. Archibald[4] has collected and made available most of the older work, with emphasis on the preparation of samples for atomic weight determinations.

It should be pointed out here that the requirements for atomic weight samples and for spectro-

* Presented at the Ninth Summer Conference on Spectroscopy and its Applications at Massachusetts Institute of Technology, July, 1941, and published with the permission of the Director of the Florida Agricultural Experiment Station.

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[1] T. A. Wright, "Report of subcommittee V on standards and pure materials," Proc. A.S.T.M. **37**, 531–7 (1937).

[2] T. A. Wright, "Superpurity metals," Proc. A.S.T.M. **37**, 538–42 (1937).

[3] T. A. Wright, "The Availability of high purity metals for spectroscopic purposes," *Spectroscopy in Science and Industry* (John Wiley & Sons, Inc., New York, 1938), pp. 47–50.

[4] E. H. Archibald, *The Preparation of Pure Inorganic Substances* (John Wiley & Sons, Inc., New York, 1932).

scopic samples are not the same. Samples for use in the determination of atomic weights should contain, as a maximum, a total impurity content which is incapable of affecting the accuracy of the determination. In many cases this requirement permits a total impurity content of about one part in ten thousand. In certain cases in which the impurity reacts similarly to the major constituent, and does not have a widely different atomic weight, the relation between impurity content and error produced is so favorable as to make a still higher impurity content unobjectionable. Thus, samples which are of adequate purity for use in the determination of atomic weights may contain significant and objectionable proportions of impurities rendering them unsuitable for spectroscopic uses. However, chemicals for spectroscopic uses need not be prepared with such extreme care as regards exclusion of moisture, or of foreign anions, and even metallic impurities may be present in detectable proportions if the sample is not to be used in analyses for these specific elements. Since there is this difference in requirements for the two types of samples, it is not safe to assume that a method which gave good results in the preparation of an atomic weight sample will give equally satisfactory results in the preparation of the same compound for spectroscopic use. Many of the older methods for purifying chemicals were developed without the aid of the presently available highly sensitive methods of analysis. Before these methods may be used with assurance, their validity requires analytical confirmation.

TABLE I. Elements included in the study, and wave-lengths employed for analyses.

Ag	3280.67 3382.89	Mg	2852.13
Al	3944.03 3961.54	Mn	4030.76 4033.07 4034.45
As	2860.46	Mo	3132.60 3902.96
B	2496.78 2497.73	Ni	3414.77
Ba	4554.04	Pb	2833.07
Be	3130.42 3131.06	Sb	2877.92
Bi	3067.73	Si	2881.59
Ca	3933.67 3968.48 4226.73	Sn	2839.99 2863.32 3262.33
Cd	3261.05	Sr	4077.71 4607.34
Co	3453.51	Ti	3370.44 3371.46 3372.80
Cr	4254.34 4274.80	Tl	5350.47
Cs	4555.26	V	4379.24 to 4408.52
Cu	3247.55 3273.96	W	4008.76
Fe	3020.65 3021.08	Y	4900.12
K	4044.16 4047.22	Zn	2138.56
La	3949.10	Zr	3496.21 3391.98
Li	4602.99		

The problem of preparing chemicals of satisfactory purity for spectroscopic purposes involves the evaluation of available methods, revision of these methods to fit them to the specific requirements of the problem, and development of new methods for those cases in which the existing methods are found unsatisfactory. Such work necessarily leads to a large proportion of negative results of no usefulness, and a relatively small proportion of successful methods. The purpose of this paper is to present a summary of such of this information as has been found useful in the preparation of certain compounds of suitably high purity. Due to limitations of space, many of the negative results obtained must be omitted; numerous references of interest, but not of direct applicability, cannot be included. Procedures to be described should be considered as suitable methods, and not as necessarily the only, or even best, methods available.

COMPOUNDS AND IMPURITIES STUDIED

The principal constituents of most material of agricultural interest are compounds of calcium, magnesium, potassium, sodium, silicon, phosphorus, sulfur, chlorine, carbon, oxygen, and nitrogen. Assuming the availability of purified compounds of these elements, it is possible to prepare standard samples suitable for use in the analysis of soil, plant, animal, and soil amendment materials, either by a "rough comparison" method, or by more exact quantitative procedures. Preparation of the standards involves

the preparation of a base material similar in composition to the samples being analyzed, and incorporation of known quantities of the elements for which analysis is being made. Such standard samples are used either for spectrographic comparison with the analytical samples by the method introduced by Nitchie,[5] or for establishing working curves for more exact quantitative methods. Rogers[6] has described the procedures used in this laboratory.

Selection of impurity elements for inclusion in this study was based upon consideration of the elements likely to be present in the type of samples for which analysis was to be made, impurities generally present in the reagent grade of chemicals available for use as starting materials, and elements present as major constituents in samples to be analyzed. It was considered unnecessary to remove this last-mentioned group of elements; however, where information concerning this group was obtainable without extra trouble, such information was recorded. Elements included in the study are listed in Table I.

METHOD OF ANALYSIS FOR IMPURITIES

In this study the spectrographic method of analysis has been most generally used, since only those impurities which are spectrographically detectable are of interest in the preparation of spectrographic standards. Occasionally, chemical methods were used to determine whether an element spectrographically indicated as present was actually a constituent of the sample, or was contributed by the graphite electrodes used.

For spectrographic analyses, a large Littrow type spectrograph, with interchangeable glass and quartz prisms, was used. Samples were volatilized completely from a drilled cavity in the lower, positive member of a pair of vertically arranged graphite electrodes by a direct current of about 9 amperes. The usual precautions as to breaking, drilling, and preburning of electrodes were observed. An image of the arc was focused sharply on the slit by means of a quartz condensing lens. A slit width of 20 microns was employed. Exposures were such as to give maximum line intensity without excessive background; lengths of exposure and quantities of samples employed were adjusted accordingly. Arcing time varied with different types of samples between two and four minutes. Spectra were recorded on suitable types of Eastman plates, which were developed, fixed, washed, and dried as recommended by the manufacturers.[7] Rough quantitative estimates of proportions of impurities present in samples were obtained by comparison with synthetic standards in the manner introduced by Nitchie.[5] However, the standards employed were known to be defective, due to the presence of impurities in the chemicals used in their preparation, and the quantitative estimates obtained were consequently in error. For purely qualitative evaluation of the effectiveness of purification procedures, it was sufficient to take samples at various stages of the process, and photograph spectra obtained from these samples successively on the same plate, along with a standard spectrum for the purpose of line identification. Examination of these spectra with a hand magnifier for changes in intensities of impurity lines from sample to sample gave a sufficiently accurate measure of the effectiveness of various purification methods.

For determination of zinc and boron, a Leiss medium quartz spectrograph was used. Details of the method of analysis were essentially as described above as used with the large Littrow instrument.

The presence of significant quantities of various impurities in graphite electrodes has caused trouble in the analysis of relatively pure samples, most especially in cases in which a "latent impurity"[8] effect occurred. The interference due to electrode impurities may be considerably reduced by the use of electrodes selected with reference to the particular elements being determined. This may require the use of two or more types of electrodes for the analysis of a single sample. The total number of impurities common to all available types of electrodes is less than the number present in any single type. Figure 1 shows the presence of barium and strontium as "latent" impurities in one type of graphite electrode, and

[5] C. C. Nitchie, "Quantitative analysis with the spectrograph," Ind. Eng. Chem. Anal. Ed. 1, 1–7 (1929).

[6] L. H. Rogers, "Spectrochemical analysis in agricultural research," J. Opt. Soc. Am. 31, 260–3 (1941).

[7] *Photographic Plates for use in Spectroscopy and Astronomy* (Eastman Kodak Company, Rochester, New York, 1940), fourth edition.

[8] D. A. Webb, "Latent impurities in electrodes used for spectrographic research," Nature 139, 248 (1937).

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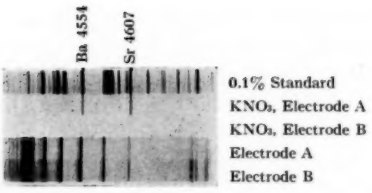


FIG. 1. Barium and strontium as electrode "latent impurities."

the absence of these elements in another type. Both types were supplied by the National Carbon Company. That identified as *A* was the Regular Spectroscopic Electrode, treated by the solvent purification method of Standen and Kovach,[9] and *B* the Special Spectroscopic Electrode. In the spectra obtained from blank exposures of these two types of electrodes, the carbon bandheads at 4606.1 and 4553.1A should not be confused with the strontium and barium lines, which are near, but distinctly separated from these bandheads.

EXTENT OF REMOVAL OF IMPURITIES

Satisfactory reduction in the impurity content of chemicals was considered to have been obtained when the impurities in question could no longer be detected by the method of analysis used. Any estimate which could be made of the proportions of impurities remaining would, in most cases, be of doubtful accuracy. Consequently, no effort will be made to indicate the degree of purity obtained, other than to specify conditions of analysis. Wave-lengths of lines employed, as given by Ryde and Jenkins,[10] for all elements other than yttrium and zinc, are listed in Table I.

PREPARATION OF PURIFIED CHEMICALS

I. Acids and Reagents

Distillation suffices for the preparation of various acids of high purity. For this purpose a Pyrex still with large (3 liter) boiling flask fitted to a condenser by means of a ground joint, and having a glass stoppered opening for the addition of liquids, is convenient. Hydrochloric acid should be distilled as a (1–1) dilution of concentrated acid with water. Nitric acid may be handled as the ordinary concentrated acid. Sulfuric acid of satisfactory purity may be purchased. Redistilled ammonium hydroxide solutions may be prepared by use of the same still, if the condenser is fitted with a suitable delivery tube, by evolution of ammonia, through gentle heating of concentrated ammonium hydroxide contained in the boiling flask. The ammonia is introduced into cold, redistilled water contained in a paraffined bottle. "Redistilled" ammonium carbonate solution may be prepared in a similar manner from ammonium carbonate and an approximately equal weight of water, placed in the boiling flask.

Large quantities of redistilled water are required for use in the various purification procedures. A still suitable for continuous operation, such as that described by Holmes,[11] is suitable for this purpose.

Purified phosphoric acid may be prepared by the use of phosphorus pentoxide as a starting material. The oxide may be sublimed along the length of a Pyrex tube. Passage of a current of dried air through the apparatus aids in the sublimation. The purified oxide may finally be sublimed into a Pyrex flask, and converted to phosphoric acid by the addition of water.

Materials prepared as described above are used either as sources of their constituent elements, or as necessary reagents or solvents required in the preparation of other compounds. Wherever the use of acids, water, ammonium hydroxide, or ammonium carbonate is specified in the descriptions of purification procedures which follow, it is understood that purified materials, prepared as described above, are used.

II. Silica

Purified silicon tetrachloride may be prepared by repeated fractional distillation. The chemical nature of this compound, and the method by which it is prepared, ensure the absence of impurities which are normally present in many other compounds of silicon. The presence of other elements which form volatile chlorides is to be expected, but those elements which form only chlorides of low volatility will ordinarily be absent. Preliminary analysis of the silicon tetrachloride which is to be purified, and consideration of the boiling points of the chlorides of the

[9] G. W. Standen and L. Kovach, Jr., "Purification of graphite electrodes for spectrochemical analysis," Proc. A.S.T.M. **35**, Pt. 2, 79–86 (1935).

[10] J. W. Ryde and H. G. Jenkins, *Sensitive Arc Lines of 50 Elements* (Adam Hilger, Ltd., London, 1935).

[11] F. E. Holmes, "Apparatus for maintaining constant levels in a water bath and a distilling flask," Ind. Eng. Chem. Anal. Ed. **12**, 483–85 (1940).

TABLE II. Preparation of purified silica by distillation of silicon tetrachloride.

Sample No.	Identification	Analysis* Ba	Cr	Mn	Al	Ca	Zr	Ag	Cu	Ti	Fe	Sb	Sn	B	Zn	Mg
1796	C.P. silicic acid	+†	−	−	+	+	+	+	+	+	+	−	−			+
4024	sea sand	+	+	+	+	+	−	−	+	+	+	−	−			+
4025	powdered sand	+	−	−	+	+	+	−	+	+	+	−	−			+
4026	washed and ignited sand	+	−	−	+	+	−	−	+	+	+	−	−			+
4276	$SiCl_4$ (Technical)	−	−	−	−	−	−	−	+	+	+	+	+	−	−	−
4277	residue from 1st distn. of No. 4276	−	−	−	−	−	−	−	+	+	+	+	+	−	−	+
4278	residue from 2nd distn. of No. 4276	−	−	−	−	−	−	−	+	+	+	+	+	−	−	+
4279	residue from 4th distn. of No. 4276	−	−	−	−	−	−	−	+	−	−	−	+	−	−	+
4280	redistilled (4X) $SiCl_4$	−	−	−	−	−	−	−	+	−	−	−	−	−	−	−

* Thallium, strontium, lithium, caesium, vanadium, yttrium, tungsten, lanthanum, cobalt, nickel, cadmium, molybdenum, beryllium, bismuth arsenic, and lead were not detected in any of these samples. Blank spaces under B and Zn indicate that the sample in question was not analyzed for these elements.

† + indicates that the element in question was detected spectrographically in the sample. − indicates that the element was not detected spectrographically in the sample.

elements present, will indicate the type of distillation required to free the silicon tetrachloride of these impurities. Thus it is determined whether the head fraction, the middle fraction, or the tail fraction should be discarded.

For this distillation a closed, all-Pyrex still which can be swept free of moisture by a current of dried air, and protected from the entrance of atmospheric moisture by a drying tube filled with a suitable drying agent, is required. An addition funnel permitting the introduction of silicon tetrachloride into the still without undue admission of atmospheric moisture is desirable. The Kahane digestion assembly (obtainable from the Scientific Glass Apparatus Company, Bloomfield, New Jersey) has been found to meet these requirements.

Table II shows the results obtained by four distillations of an initially rather impure sample of silicon tetrachloride. Analyses of several other compounds of silicon are included for purposes of comparison. At each distillation of this sample of silicon tetrachloride, the last-boiling tenth of the material was removed from the boiling flask, and reserved for conversion to silica and analysis. The distillate, consisting of about nine-tenths of the starting material, was reserved for distillation; until after the fourth distillation, the distillate was also reserved for conversion to silica.

These samples were converted to silica by pouring into cold water contained in a silica dish cooled in an ice bath, followed by evaporation to dryness on the water bath, and final ignition at 1200°C. These samples were homogenized in an agate mortar and analyzed spectrographically.

Since all impurities which had been detected in the starting material were found to be concentrated in the last boiling fractions, it was believed that analyses of these samples would give the best indication of satisfactory purity of the main fraction. Figure 2 shows portions of the spectra of various samples obtained by this process. The material prepared by this method (sample No. 4280, Table II) contained no impurities detectable by the method of spectrographic analysis employed, other than copper. The apparent presence of copper in this sample was probably due to the presence of copper in the graphite electrodes used for the analyses.

Vacuum distillation of silicon tetrachloride has been quite generally used in the preparation of material for the determination of the atomic weight of silicon.[12] Details of the method generally employed and references to the original literature are given by Archibald.[4]

III. Calcium Compounds

Two methods will be described for the preparation of purified calcium compounds. The comparative convenience of these methods will depend upon the equipment available and the quantity of material required. The method to be described first, which involves the removal of certain impurities by repeated extraction of calcium hydroxide with water, under conditions ensuring absence of carbon dioxide, is recommended if a muffle furnace capable of maintaining a temperature of 1300°C is available, and for the preparation of small quantities of material. The other method, involving repeated recrystalliza-

[12] P. F. Weatherill and P. S. Brundage, "A revision of the atomic weight of silicon. The ratio $SiCl_4 : SiO_2$," J. Am. Chem. Soc. **54**, 3932–8 (1932).

tion of calcium sulfate, is probably best for production of larger quantities.

Strontium and barium are the most difficultly removable impurities found in calcium compounds. The universal occurrence of strontium in all sources of calcium has been indicated.[13] In this laboratory, no compounds of calcium have ever been found which were free of spectrographically detectable proportions of strontium, except for samples prepared by the methods to be described.

Due to the difficulty of removing strontium and barium, preliminary analysis for the purpose of selecting a starting material which is low in these elements is especially important. A desirable material is one which contains less than 0.01 percent of strontium, and no detectable barium. Of the various compounds which have been examined (oxide, carbonate, chloride, nitrate, and sulfate), reagent grade calcium sulfate has been found to meet these requirements most frequently, while the nitrate is probably next best, and the oxide and carbonate are very unsatisfactory.

If the removal of strontium is to be effected by extraction of calcium hydroxide, barium, if present, should be removed by repeated precipitation of the calcium as the oxalate, or if the starting material is the chloride, by crystallization, with successive discard of five small head fractions of crystals, each comprising about 1 percent of the amount of calcium chloride being used. Crystallization may be carried out from an aqueous solution of calcium chloride, saturated at room temperature, by gradual cooling. Each fraction of crystals may be separated from the mother liquor by decantation. A marked reduction in barium content of the calcium chloride contained in the mother liquor to somewhat less than 0.001 percent is secured by this process, but beyond this level further crystallization is not effective.

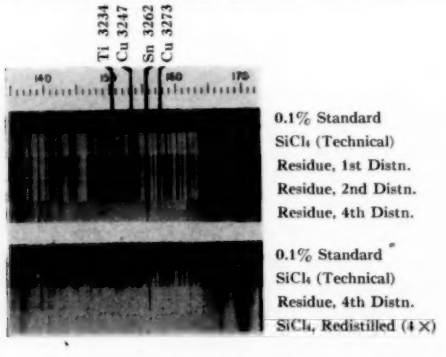


FIG. 2. Preparation of purified silica by distillation of silicon tetrachloride.

It is believed that this process involves the trapping of colloidal barium sulfate by the calcium chloride crystals, and consequent reduction of the barium content to the limit of true solubility of barium sulfate in the solution, although no positive supporting evidence can be offered.

Additional reduction of the barium content to a level below that of spectrographic detectability may be secured by double precipitation of the calcium as the oxalate. In making these precipitations, the calcium chloride solution should be diluted to give a concentration of about 100 grams of calcium oxide per liter of solution. Heat the solution to 90°C and add a twofold excess of ammonium oxalate and sufficient hydrochloric acid to keep the calcium oxalate in solution. Add ammonium hydroxide (10–15 percent NH_3) slowly, with constant stirring, until a very faint turbidity is produced. Digest the solution at about 90°C for 30 minutes. Add a few drops of methyl red indicator solution, and then continue the addition of ammonium hydroxide, slowly, and with stirring, until the methyl red end point is reached. Digest the solution for about 15 minutes, and then filter off the precipitate on a Pyrex fritted filter. Discard the filtrate, dissolve the precipitate in acidified water, and return the solution to a clean beaker. Precipitate the calcium as oxalate in the same manner as before (it is not necessary to add more ammonium oxalate), and again filter off the purified calcium oxalate. Wash the precipitate very thoroughly with warm water, in order to remove chlorides. Dry the barium-free calcium oxalate, transfer it to a platinum container, preferably a shallow dish, and ignite at 1300°C, for 2 hours, or longer, for complete conversion of the oxalate to oxide. (Note: If chlorides were not thoroughly washed out of the oxalate precipitate, the platinum dish will be seriously damaged by free chlorine which will be formed during the ignition.) Cool the ignited oxide in a desiccator, over fused sodium hydroxide, to prevent the reformation of carbonate.

[13] W. Noll, "Geochemistry of strontium," Chem. Erde **8**, 507–600 (1934).

Empty the cooled oxide into a glass-stoppered container (Pyrex) containing water which has been boiled to remove carbon dioxide. The ratio of weight of water to weight of calcium oxide should be about 50–1. Stopper the container as soon as the violent reaction has ceased, and allow it to stand from 12 to 24 hours. Decant the supernatant liquid from the calcium hydroxide, as completely as possible, transfer the hydroxide back to the platinum container, dry, and reignite as before. Repeat the extraction with water again in the same manner. The hydroxide should now contain no detectable strontium, but should be analyzed, and again treated, if strontium is detected.

When the calcium hydroxide has been freed of detectable strontium, it may be converted to chloride by addition of hydrochloric acid, the solution evaporated to dryness, preferably in a platinum or silica container, and the chloride baked at 120°C for 1–2 hours, dissolved in water, and filtered to remove objectionable quantities of silica.

The resulting chloride should now be of satisfactory purity as regards barium and strontium, but may contain numerous other impurities, including platinum and alkali metal salts derived from the containers used for the above described treatment, in addition to impurities present in the starting material. Treatment to remove many of these impurities will be described later.

Satisfactory removal of both barium and strontium is obtained by repeated recrystallization of calcium sulfate from hot, 2–3 *N* hydrochloric acid solution. Magnesium is also effectively removed by this method. Calcium sulfate is the most convenient starting material, but if the sulfate is not available, it may conveniently be prepared from the chloride or nitrate in the following manner: Add 15 liters of 2.5 *N* hydrochloric acid solution to a 5-gallon Pyrex bottle. Place the bottle in a water bath and heat the solution to 90–95°C. Add about 1 liter of a saturated (20–25°C) solution of calcium chloride or nitrate. Add slowly, with stirring, 1 liter of sulfuric acid (1–1). Allow the solution to cool to room temperature, filter off the crop of calcium sulfate crystals on a large Büchner funnel (no filter paper is needed, due to the large size of the crystals), pack the crystals down in the filter by use of a porcelain spatula, and draw off the mother liquor as completely as possible, by use of a filter pump. Wash the crystals once, and again remove excess water. Store the damp calcium sulfate in a suitable container for future use. The mother liquor may be reused several times. In this procedure it is necessary that the formation of partially dehydrated, difficultly soluble calcium sulfate be avoided. The addition of sulfuric acid must be slow, and must be accompanied by vigorous stirring. With these precautions, it should be possible to add the specified quantity of sulfuric acid without the formation of a permanent precipitate or the appearance of permanent turbidity. The appearance of turbidity during the addition of sulfuric acid, if such turbidity does not disappear by the time all the acid has been added, is evidence of the formation of dehydrated calcium sulfate. Such crops of material should be discarded. Normally, no precipitate should appear until several minutes after all the sulfuric acid has been added.

For recrystallizing calcium sulfate, 5-gallon Pyrex bottles containing about 15 liters of 2.5 *N* hydrochloric acid are used. Ten bottles, numbered consecutively from 1 to 10, are required. Place the number 1 bottle in a water bath, and heat the solution which it contains to maximum temperature (90–95°C). Add calcium sulfate, with vigorous stirring, until the solution is nearly saturated, as evidenced by decreased rate of solution of the calcium sulfate.

Permit the solution to cool overnight. Filter off the crystals which separate (about half the quantity initially added) on a Büchner funnel, pack the mass of crystals down with a porcelain spatula, and drain off the mother liquor as completely as possible by use of a filter pump. Use the mother liquor for dissolving and crystallizing a second portion of calcium sulfate. Saturate the solution in the number 2 bottle with the first two crops of crystals from the number 1 bottle, the number 3 solution with the first two crops of crystals from the number 2 bottle, continuing in this manner until the first crop of crystals is obtained from the number 10 solution. Throughout this process, details of solution, crystallization, and separation of crystals are carried out as described for the number 1 bottle. Covered glass

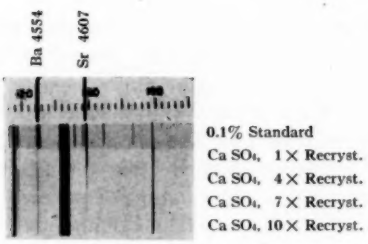


FIG. 3. Removal of strontium from calcium sulfate by recrystallization.

containers of 3–4 liters capacity are useful for temporary storage of calcium sulfate.

By beginning work each day with the material of highest purity, and working toward successively less pure material, the necessity for washing apparatus is almost entirely avoided. The first crop of crystals from the number 10 solution should be analyzed. It should contain no detectable proportion of either strontium or barium. Likewise, each following crop of calcium sulfate from the number 10 solution should be analyzed. The first crop which is found to contain detectable proportions of strontium should be reserved; it, and the following crop should be used for saturating a fresh solution. At this time, discard the number 1 solution, so as to retain a total of ten solutions. Addition of fresh solutions to the series and discard of the most impure solution must be controlled by analysis, so as to give the desired results. Although this procedure is obviously somewhat tedious and requires the expenditure of considerable time before the first purified material is obtained, the quality of the product is very high. Figure 3 illustrates the removal of strontium by this method.

Rubber stoppers, if used for fitting the Büchner funnel to the receiving bottle, should be replaced frequently; otherwise, by disintegration, they may introduce barium contamination.*

The effectiveness of recrystallization of calcium sulfate for the removal of barium and strontium is probably due to several factors, including the compactness and consequent low deformability of the sulfate ion[14] and the large ratio of solvent to solute. It will be noticed, if the barium and strontium content of a batch of calcium sulfate is followed through the entire process, that considerations of relative solubility do not apply to this process. The most insoluble element, barium, is concentrated most rapidly in the mother liquor; in keeping with its greater ionic radius, and smaller ionic potential (as compared with strontium and calcium), it appears to enter into the calcium sulfate crystal less readily than does strontium. The low strontium content of calcium sulfate formed by deposition from sea water, as compared with the relatively higher strontium content of sea water,[13] has furnished an indication that this separation should be good.

Calcium sulfate may be converted into the carbonate by treatment with ammonium carbonate solution.[15] The carbonate may in turn be converted into nitrate or chloride by treatment with acid.

Having now obtained calcium chloride of low barium and strontium content, other impurities may be removed by any one of several methods. Richards and Hönigschmid[15] have described a method for the removal of iron, aluminum, and magnesium by treatment of the chloride or nitrate solution with "milk of lime" to cause precipitation of the hydroxides of these elements. Steinberg[16] has described a method which involves precipitation of heavy metals by coprecipitation with calcium carbonate. In either of these methods, the hydroxide or carbonate should be prepared from a portion of the sample being treated, to avoid reintroduction of barium and strontium. The carbonate may conveniently be prepared in the solution which is being treated, by addition of ammonium carbonate. In this manner, several small fractions of calcium carbonate may be precipitated in the solution being treated, each fraction being removed by filtration. This procedure is carried out in a boiling solution.

For the removal of certain metals, extraction of a solution of calcium chloride, made slightly alkaline by the addition of a few drops of ammonium hydroxide, with a solution of dithizone in chloroform, yields excellent results. This method for preparing purified compounds has

* I am indebted to Mr. R. A. Carrigan, of this laboratory, for this solution to a rather puzzling case of accidental contamination.

[14] V. M. Goldschmidt, "The principles of distribution of chemical elements in minerals and rocks," J. Chem. Soc. **1937**, pp. 655–673.

[15] T. W. Richards and Otto Hönigschmid, "A revision of the atomic weight of calcium," J. Am. Chem. Soc. **32**, 1577–90 (1910).

[16] R. A. Steinberg, "Nutrient solution purification for removal of heavy metals in deficiency investigations with Aspergillus niger," J. Agr. Research **51**, 413–24 (1935).

been patented.[17] It has been found very effective for the removal of copper and zinc. The solution of dithizone should be prepared and purified as recommended by Winkler[18] or by other suitable methods.

By suitable combination of the methods described above, calcium compounds of satisfactory purity for spectroscopic use may be prepared. If a compound other than the chloride is required, the chloride may be converted to carbonate by treatment with ammonium carbonate, and from the carbonate any desired compound may be prepared.

IV. Magnesium Compounds

Magnesium compounds which are free of detectable proportions of barium and strontium occur with sufficient frequency to make a search for such a compound profitable, if freedom from these impurities is required. Magnesium chloride makes a good starting material for the preparation of purified magnesium oxide. It is converted to the oxychloride by gentle ignition in a silica or platinum container, followed by leaching with water, as described for the treatment of calcium oxide. The ignition should be made at a temperature not exceeding about 500°C, to avoid excessive attack on the container. Barium and strontium, if originally present, will be partially eliminated by this treatment.

Richards and Parker[19] have used a method involving the same principle for the removal of sodium and potassium from magnesium compounds. No data have been obtained in this laboratory on the effectiveness of the method for the removal of sodium and potassium. Prior to conversion to the oxide, numerous other impurities may be removed by treatment of a solution of the chloride with basic magnesium carbonate[16] or by use of dithizone, as described for the treatment of calcium chloride.

Recrystallization of magnesium sulfate from hot sulfuric acid solution is very effective for the removal of barium and strontium. Ordinarily, for this method, the starting material will be magnesium chloride or magnesium sulfate. In either case, a saturated aqueous solution (room temperature) is prepared. An equal volume of concentrated sulfuric acid is added, and the solution is boiled to remove water. Constant stirring is required to prevent bumping. When about half the water present has been evaporated off, most of the magnesium present will have been deposited as a dense, crystalline precipitate of sulfate. This precipitate is filtered off on a Pyrex fritted filter, and drained by use of a filter pump. The precipitate is transferred to a Pyrex beaker, and dissolved in the minimum possible quantity of hot water. Reprecipitation is then effected by addition of sulfuric acid followed by evaporation, as before.

This treatment may be repeated as many times as is indicated by analysis to be necessary; however, four crystallizations should be sufficient. The presence of turbidity in the hot aqueous solution at any time prior to evaporation is an indication of the presence of an excessive amount of barium. Such turbidity should be removed by filtration before continuing with the treatment, otherwise barium will not be removed. Figure 4 shows the rapidity with which strontium is removed, and likewise the failure of barium to be removed until an insoluble precipitate of barium sulfate was filtered off, prior to the fifth precipitation.

When the product is of the required purity, as shown by analysis, it may be freed of water and sulfuric acid by ignition in platinum or silica at a temperature of about 400°C. The resulting product is anhydrous magnesium sulfate. Other impurities than barium and strontium may be removed as has already been indicated for magnesium chloride.

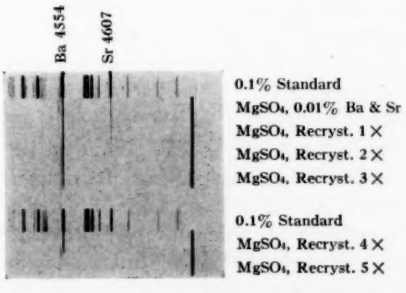


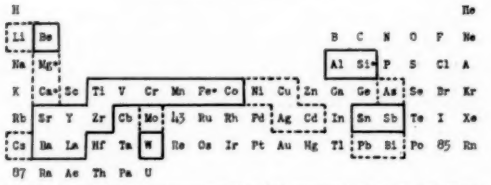
FIG. 4. Removal of strontium and barium from magnesium sulfate by recrystallization from sulfuric acid solution.

[17] Siemens & Halske A.-G., (Hellmut Fischer, inventor) Ger. 628,078, March 28, 1936 (Cl. 12g. 1.01) Refining Chemical Elements and Compounds.

[18] W. O. Winkler, "Determination of small quantities of mercury in leafy vegetables by means of diphenylthiocarbazone," J. Assn. Official Agr. Chem. **18**, 638–44 (1938).

[19] T. W. Richards and H. G. Parker, "A revision of the atomic weight of magnesium," Proc. Am. Acad. **32**, 55–73 (1896).

TABLE III. Removal of various elements from potassium chloride by distillation.



Solid blocks indicate elements which are removed from the distillate. Broken blocks indicate elements which are not removed from the distillate.
* Results for magnesium, calcium, silicon, and iron are uncertain, due to interference by electrode impurities.

V. Sodium and Potassium Compounds

The preparation of purified compounds of sodium and potassium may be carried out by identical methods. For the removal of many impurities, repeated volatilization of the alkali chloride at a temperature of 900–1000°C has been found effective. A "still" for this purpose may be improvised from a platinum or porcelain crucible, a porcelain ring, and a Pyrex flask. The porcelain ring should be of such size that it will fit tightly around the top of the crucible. The open end of the Pyrex flask is fitted against the open end of the crucible. The porcelain ring serves as a support for the assembly, as well as protecting the flask from the source of heat applied to the crucible.

In use, the crucible is partly filled with the alkali chloride to be purified, and the still assembled in an inclined position (inclination of the still permits air to circulate in such a manner as to aid in the deposition of the condensate on the side of the flask). The crucible is heated by a blast lamp flame, or in any convenient manner capable of maintaining the contents of the crucible at a temperature of not less than 900°C. The charge of alkali chloride melts and vaporizes. The vapor condenses to a fine powder at a short distance above the surface of the liquid. Circulating air currents deposit the powder upon the sides of the flask.

When volatilization of the charge has been nearly completed, the still is permitted to cool, taken apart with care to prevent dislodging of the condensate from the flask, and the condensate transferred to a suitable container. Revolatilization, one or more additional times, may be required to give a product of satisfactory purity. The efficiency of removal of various impurities from potassium chloride, to which 0.1 percent of each element (added as oxide, carbonate, or chloride) had been added, by three successive volatilizations, is indicated in Table III. Following volatilization, dithizone extraction is useful for removal of several elements which are not efficiently removed by volatilization, as well as platinum introduced during the volatilization.

Crystallization of the alkali chloride from the extracted solution is conveniently effected by saturating the solution with hydrogen chloride gas. The precipitated chloride should be filtered off, washed sparingly, and dried at about 500°C.

Strontium is very efficiently removed from a solution (10 percent) of potassium nitrate by addition of strontium-free calcium nitrate followed by precipitation of the calcium as oxalate. This method is effective for reducing the strontium content considerably below the lower limit of spectrographic detectability, as evidenced by the appearance of readily detectable proportions of strontium in the calcium oxalate precipitates from solutions of potassium nitrate in which strontium could not be detected. Noll[13] has used a single calcium oxalate precipitation for concentration of strontium to permit its determination in potassium compounds.

It will be noted from Fig. 5 that a single treatment leaves some strontium which may be further reduced by additional treatments. For this reason, it is recommended that treatment with small portions (about ½ percent of the quantity of potassium nitrate being treated) of calcium nitrate be repeated until strontium is barely detectable in the calcium oxalate residue. This will normally require four or five treatments. Barium is not effectively removed by this treatment.

TABLE IV. Removal of heavy metals from potassium nitrate solution by basic magnesium carbonate treatment.

Elements removed by one treatment	Elements reduced in concentration by repeated treatment	Elements not effectively removed
Al	Ag	B
Co	Cu	Mo
Cr	Zn	
Mn		
Ni	Concentration of potassium nitrate: 100 g/l.	
Pb	Concentration of each heavy metal: 0.0001 g/l.	
Sn	Basic magnesium carbonate: 0.5 g/l.	
Ti		
V		

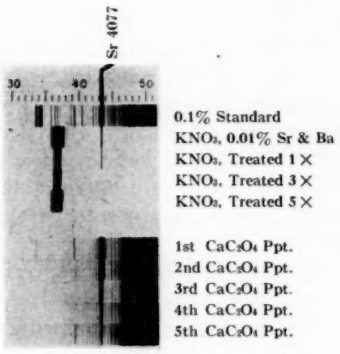


FIG. 5. Removal of strontium from potassium nitrate solution by coprecipitation with calcium oxalate.

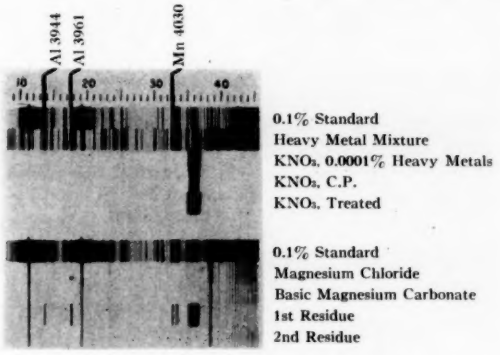


FIG. 6. Removal of heavy metals from potassium nitrate solution by basic magnesium carbonate treatment.

Following the last precipitation, the solution should be held at a temperature of 0–10°C for several hours before being filtered. This reduces the calcium content of the potassium chloride to a level below that ordinarily found in potassium compounds. However, it has not been possible to determine with certainty how effectively calcium is removed, due to interference in analyses by calcium present in all graphite electrodes obtainable.

Steinberg has described a highly satisfactory method for the removal of heavy metals from solutions by treatment with basic magnesium carbonate, and has indicated that the concentration of zinc in treated solutions may be as low as approximately one part per billion of solution.[16]

The results of some trials of this method for removal of several elements in addition to manganese, copper, iron, and zinc mentioned by Steinberg, are listed in Table IV. For these tests a solution containing 100 grams of potassium nitrate and 0.0001 gram per liter of each of the elements studied was prepared. A liter of this solution was boiled for twenty minutes with ½ gram of basic magnesium carbonate, and then immediately filtered through a Pyrex fritted filter. The filtrate was retreated several times in the same manner with fresh portions of basic magnesium carbonate. Samples were taken of the filtrates and of the residues, and were analyzed spectrographically.

The sample of basic magnesium carbonate employed was prepared from an especially pure sample of magnesium chloride, which was itself first treated with basic magnesium carbonate before being converted into basic carbonate. This gave a sample of basic magnesium carbonate which contained no spectrographically detectable proportions of heavy metals other than faint traces of iron, aluminum, and copper, which were believed to have been due to electrode impurities. Figures 6 and 7 show the manner in which some of the test elements were concentrated in the residues. Several elements appeared in decreasing proportions in the successive residues, indicating ineffective concentration of these elements in the residue. Other elements appeared only in the first (or at most the first and second) residue, indicating that these elements are very effectively concentrated in the residue from the first treatment.

The data presented in Table IV and Figs. 6 and 7 represent the results obtained in a single set of experiments only, and under the specified conditions; hence, they must not be interpreted as being generally applicable under all conditions.

It is evident that factors such as the exact composition of the solution treated, exact conditions of treatment, and specific sample of basic magnesium carbonate used may affect the results obtained. In the use of this method, it is recommended that the effectiveness of treatment be determined by analysis of the basic magnesium carbonate used and analyses of the residues from treatment. Treatment should then be repeated until analysis of the residue indicates satisfactory reduction in impurity content of the sample being purified.

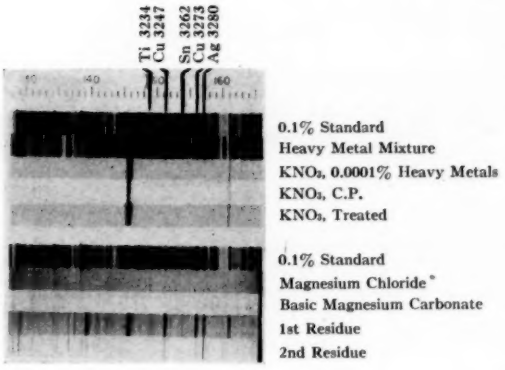


FIG. 7. Removal of heavy metals from potassium nitrate solution by basic magnesium carbonate treatment.

COMPARISON OF METHODS

The choice of methods for any particular purification problem will depend upon the impurities to be removed, the extent to which they must be removed, equipment available, and quantity of material which must be prepared. It is generally desirable to prepare a suitable quality of material in the required quantity, at the minimum expense. With this in mind, some characteristics of various methods will be indicated.

Wherever applicable, distillation has been found to give a highly pure product, either in large or small quantity, at a minimum of expense either in time or equipment. Consideration of boiling points and vapor pressures of compounds involved will allow a prediction to be made in advance as to the efficiency of purification.

Extraction procedures involving liquid-liquid extractions have been found extremely efficient, rapid, and cheap. Although the use of dithizone has been stressed, other reagents have been found equally effective. For selecting reagents and solvents for specific separations, reference to one of the several compilations on the use of organic reagents, such as "Table of Reagents,"[20] is of value.

Extraction of solid materials with liquids is of limited applicability but is satisfactory in certain cases. Of the cases studied, it has given good results only in those in which the elements to be removed are present as compounds of high solubility as compared to the major constituent, and where the material being extracted reacts with the solvent to give an extremely finely divided product. In other cases, where treatment of crystalline material of large particle size has been attempted, and where no reaction occurs during the extraction, unsatisfactory results have been obtained.

The usefulness of adsorption or coprecipitation methods has been sufficiently indicated elsewhere.[16] The previously reported effectiveness and convenience of this method have been fully confirmed.

Recrystallization methods are to be recommended only as a last resort. Frequently, these methods have been found ineffective, expensive in time, and wasteful of material. However, if this method must be used, careful consideration should be given to the various factors involved in the separation: the relative atomic radii and ionic potentials of the various elements, compactness of anion involved, solvent composition and *p*H, solubility of the major constituent in the proposed solvent, and exact conditions under which crystallization is effected. Trial and error study of procedures which appear most promising is then indicated.

SUMMARY

The need for specially purified compounds for use in the preparation of standards for spectrographic analysis of agricultural materials has been indicated, and the special requirements which these compounds should meet have been emphasized.

Suitable methods for the preparation of purified compounds of magnesium, calcium, potassium, sodium, and silicon have been described in detail.

The relative efficiency, convenience, and cost of various methods has been compared, and the probable usefulness of other methods has been indicated.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Mr. L. H. Rogers, Mr. R. A. Carrigan, and Dr. L. W. Gaddum for much assistance and numerous helpful suggestions given during the course of this work.

[20] International Committee on New Analytical Reactions and Reagents, *Tables of Reagents for Inorganic Analysis* (Akademische Verlagsgesellschaft m. b. h., Leipzig, 1938).